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DEVELOPMENT OF PROTECTIVE
FINISHES FOR GLASS MONOFILAMENTS

by

J. Shulman, S. L. Kaplan, and H. P. Beutner

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ARTHUR D. LITTLE, INC.
CAMBRIDGE, MASS.

Final Report

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Prepared for

National Aeronautics and Space Administration

March 3, 1966

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Chemical Rocket Division
R. F. LARK

Arthur D. Little, Inc.
Cambridge, Mass.

Development of Protective Finishes
for Glass Monofilament

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J. Shulman, S. L. Kaplan, and H. P. Beutner

Arthur D. Little, Inc.

ABSTRACT

Several organic finishes and a nickel-metal finish have been studied to determine their effect in preventing degradation of the strength of glass filaments in resin-glass composites. "HTS-Simulated" finish glass was used as the control in comparing the new finishes. Laboratory apparatus was assembled for continuously applying nickel to the glass filament as it was being drawn from the bushing.

ACKNOWLEDGEMENT

Arthur D.Little,Inc.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

Arthur D.Little,Inc.

I. SUMMARY

A. PURPOSE AND SCOPE

The objective of this study was to develop improved finishes and finishing techniques that would prevent degradation of the strength of glass filaments in resin-glass fiber composites. Several organic finishes and a nickel-metal finish were studied to determine their effect in preventing degradation of the strength of glass filaments in resin-glass composites. Simulated HTS-finish glass was used as the control in comparing the new finishes. Laboratory apparatus was assembled for continuously applying nickel to the glass filament as it was being drawn from the bushing.

B. GENERAL FINDINGS

1. On the basis of the various screening techniques used during the present study and a review of the pertinent literature, single-property tests at best provide only crude guidelines for the composite behavior of glass-fiber-resin composites in view of the complex interaction of such properties in the composite.

2. Despite the complexity of the system it is believed that intrinsic properties of the resin matrix with respect to moisture resistance (and resistance to boil test) are dominant as far as moisture resistance of a composite is concerned, provided that the resin-glass-fiber interface is essentially free from physical defects. (See, for example, SPE Journal, 19 (4) 1963, Table I, p. 380 where sample 4 shows a 65% strength retention after 12-hour boil for a composite without finish.) However, good finishes obviously are important for handling prior to composite manufacture (moisture and abrasion protection) and finishes such as the HTS finish provide reliable performance with respect to moisture resistance as well as high intrinsic composite strength.

3. It is believed that interlaminar shear strength testing provides the most reliable basis for evaluation of moisture resistance of glass-fiber-resin composites.

4. It is believed that single-cycle cryogenic tests of filament-wound composite specimens, such as tensile and interlaminar shear strengths, will yield higher strength values than those obtained at ambient temperature. However, such single-cycle tests are not necessarily indicative of long cycle life.

1

5. The possibility of improving composite behavior by the use of elastomeric materials as a finish to attenuate strain on the resin could not be positively shown. However, further exploration of this approach may be worthwhile.

C. SPECIFIC FINDINGS

1. <u>Tensile test of composite E-glass monofilament-wound NOL rings</u>. Figure A summarizes findings on NOL ring tensile tests for some selected organic finishes and the newly developed nickel finish. In spite of the large scatter of results some general observations can be made. All tests made at room temperature appear to be within the same range. Composites made from HTS finished rovings during the study appeared to fall within the same range. For comparison, some results from NASA Technical Note TN D-2741 are given which again are within a similar range.

Cryogenic tests tend to be equal to or better than room temperature tests with the possible exception of the urethane-finished composites. All finishes tended to give somewhat better boil resistance than the control series.

2. <u>Interlaminar Shear Strength Tests</u>. Figure B summarizes the interlaminar shear strength tests for composites with nickel-coated filaments, HTS-type finished filaments, and controls without finish. The HTS-type finish shows least deterioration on boil test. Nickel coatings show definite improvement over unfinished composites. Inspection of Figure 24 shows that the sample without finish was visibly frayed after prolonged boiling, while the nickel-coated specimen was physically intact even though measurably weakened as measured by an interlaminar shear strength test.

3. The feasibility of nickel coating from nickel carbonyl as an integral step in fiber drawing was demonstrated. Coatings as thin as about 20°A were apparently coherent and continuous and proved to have usefulness as a finish.

D. RECOMMENDATIONS

It is recommended that nickel-finished fiber-glass composites be further studied. Influence of coating thickness and compatibility with selected epoxy matrices of proven merit should be investigated. Low-temperature cycling tests should be undertaken to evaluate whether metallic finishes perform better than organic finishes in this type of usage.

2

LEGEND: C = No Finish, B = Buton Silane, U = Urethane, C' = No Finish Control for
Nickel Series, RT = Room Temperature, CR - Cryogenic Temperature (-320 °F),
B = Boil Test

FIGURE A   SUMMARY OF NOL RING TENSILE TESTS

3

20

Interlaminar Shear Strength x 10^3 psi

15

10

5

0

| RT | CR | | | 5 hrs |
Boil

No-Finish Control

| RT | CR | ½ | 3 | 5 | hrs |
Boil

.3-1.2% Ni
Coated

| RT | | | 3 | 6 | 24 | hrs |
Boil

HTS-Simulated

FIGURE B   SUMMARY OF INTERLAMINAR SHEAR STRENGTH
             TESTING OF MONOFILAMENT-WOUND E-GLASS
             NOL RING SEGMENTS

4

II. INTRODUCTION

The objective of this study was to develop improved finishes and finishing techniques that would prevent degradation of the strength of glass filaments in resin-glass fiber composites.

Finishes or coatings are commonly used in the fabrication of glass fiber-resin composites for the dual purpose of protecting the fibers during the entire processing operation and promoting effective bonding and protection of the fibers in the completed composites. The HTS* finish represents one of the most advanced present standards, particularly for filament-wound structures, and provides excellent handling protection of the fibers during fabrication and moisture resistance of the composites. However, present composites having ambient temperature tensile strengths (NOL test) of up to 3×10^5 psi are still somewhat short of theoretically possible values of about 4.5×10^5 psi (based on a virgin strength for E-glass monofilaments of about 5×10^5 psi). Further improvements in moisture resistance and resistance to cycling through cryogenic temperatues are also deemed desirable.

There is extensive literature and intensive continuing work dealing with the strength behavior of glass fiber-resin composites. It is clear that their behavior is not uniquely controlled by any given parameter. Many factors contribute to their overall behavior: intrinsic strength and elastic behavior of the resin matrix, resistance of the matrix to moisture and low-temperature cycling, intrinsic strength and aging behavior of the glass fiber, resin content and distribution (e.g., controlled by wetting characteristics and fabrication technique), adhesion between fibers and matrix, porosity (e.g., controlled by wetting and fabrication techniques), and resistance of the fiber-matrix bond (with or without the use of a finish) to moisture and stress under temperature cycling conditions.

Although the behavior of such composites is far from completely understood and, in particular, precise guidelines for tailoring composite properties are missing, a plausible explanation of some of the major performance characteristics seems to be emerging. It would seem from the literature, and by the experience gained in this study, that the resin matrix is, as it were, the weakest link in the chain. For example, the effect of moisture seems not only to be greatest on the resin, but to be greatly accelerated if the resin surface available to water attack is increased by inherent porosity (continuous pores) or by a weakening of the fiber-finish-resin interfaces. Composites having no finish or "poor" finishes, deteriorate much more than can be attributed to the moisture deterioration of E-glass.

---

*"High Tensile Strength" glass filament finish developed by the Owens-Corning Fiberglas Corp.

5

In the present study, attempts were made to obtain an insight into the role of finishes through the use of screening tests and monofilament-wound NOL rings. Although certain qualitative insights were obtained, even a semi-quantitative interpretation was frustrated by the dominance of resin behavior and uncontrollable factors in fabrication as experienced in the tensile NOL ring tests used for some of the final evaluations. As evidenced by work in the last period of the study, interlaminar shear strength tests might have proven vastly superior for qualifying tests, and it is believed that these tests should be used extensively in future studies of the behavior of the resin-finish-fiber interface system. Perhaps also greater emphasis should be put on the selection of resins as matrix materials which have minimal changes (both reversible and irreversible) under moisture (and boil) and cryogenic cycling conditions.

6

III. PROCESSING AND TEST EQUIPMENT

A. MONOFILAMENT GLASS-DRAWING APPARATUS

As a first step in our experimental glass-fiber coating operation, a small furnace (Figure 1) was constructed with a platinum-10% rhodium crucible heated by a refractory-insulated wound resistance wire. The crucible orifice is 0.050 inch in diameter. Conical-shaped crucibles were used since this design resulted in quite uniform temperatures throughout the crucibles. Temperature control was more or less conventional; a platinum-10% rhodium thermocouple detected the temperature near the drawing tip. Temperature control was maintained with a Leeds & Northrup silicon control rectifier unit. After early tests with Kanthal wire, platinum-10% rhodium wire was used for all experimental runs.

Since each glass-drawing furnace has its own inherent characteristics, it was necessary to vary the drawing speeds, temperature, and glass "fining" (i.e., holding at a relatively high temperature to remove gases) to obtain optimum tensile strength glass. Tensile strength of the glass increased with increased melt temperatures (up to a point). The strongest glass was obtained by holding the melt at the limit temperature of the resistance wire winding (2600°F) for two hours and then decreasing the temperature to obtain the desired drawing conditions. To prevent glass devitrification, a two-zone furnace was used which allowed the cone and tip temperature to be controlled independently and at a lower temperature than the major portion of the melt (Figure 2). To control the fiber diameter to around 10 microns, the tip temperature was held at about 2100°F. The tip temperature was controlled manually and checked periodically with an optical pyrometer. For best results in obtaining high tensile glass, it is necessary to maintain the glass melt at 2600°F for about two hours to eliminate any entrapped gases and water vapor. Further, as previously stated, the glass remains liquid at this temperature, thus preventing divitrification (which may occur at lower temperatures) resulting in reduced tensile strength glass.

B. APPLICATION OF ORGANIC FINISHES

Various methods of applying the finish to the glass filaments and the resin matrix to finished or unfinished fibers were tried. Two common industrial methods of application, a driven coating drum and reservoir impregnation, were considered and found unsuitable. The drum method required such high drum speeds to prevent fiber drag and breakage that startup was exceedingly difficult. The reservoir impregnation method could not be used for the fibers were too fragile to be dipped in and out of a bath. Vapor-phase coating was also considered; however, many of the polymeric materials being screened for potential

7

Thermocouple

1-1/8"
Insulation

4"

2"

1-3/4"

Power Source

Operating Level of
Glass Melt is 3 to
3-1/4" from Tip

1-1/2"

Orifice 0.050" dia.

One Zone

Thermocouple

1-1/8"
Insulation

4"

2"

1-3/4"

Power Source

Operating Level of
Glass Melt is 3 to
3-1/4" from Tip

Power Source

1-1/2"

Orifice 0.050" dia.
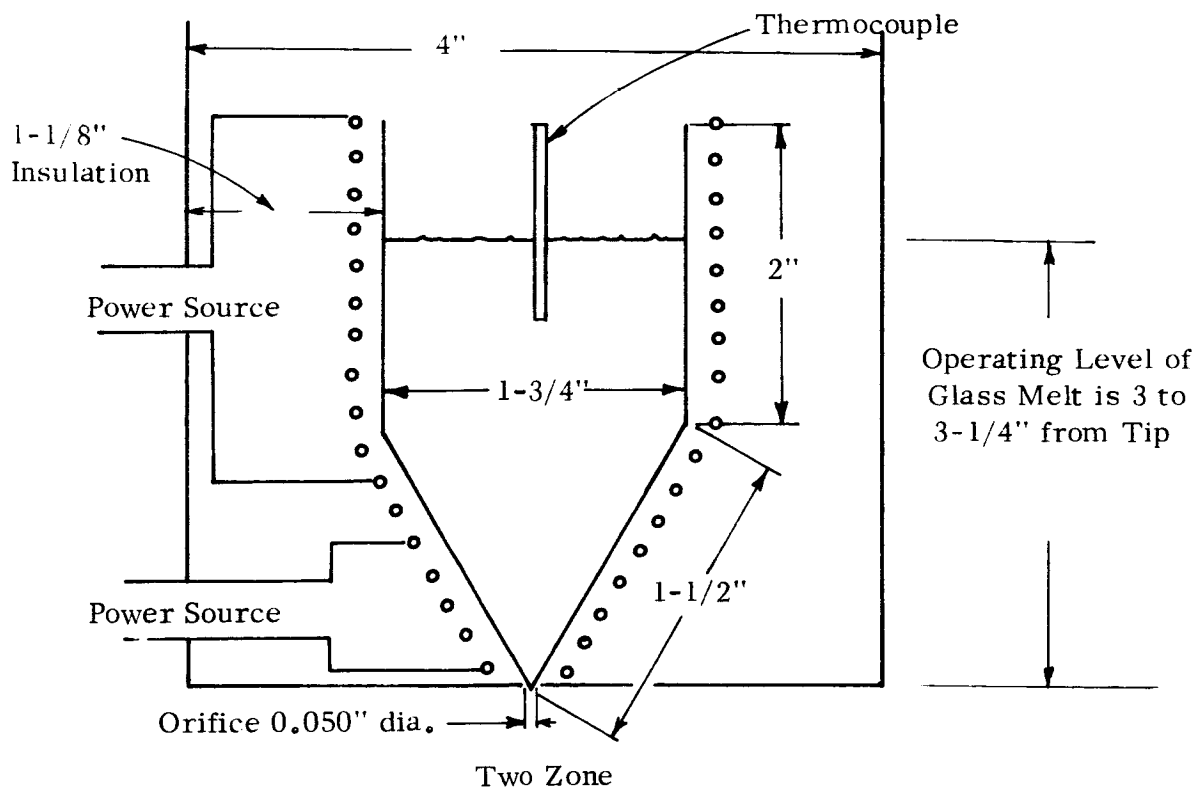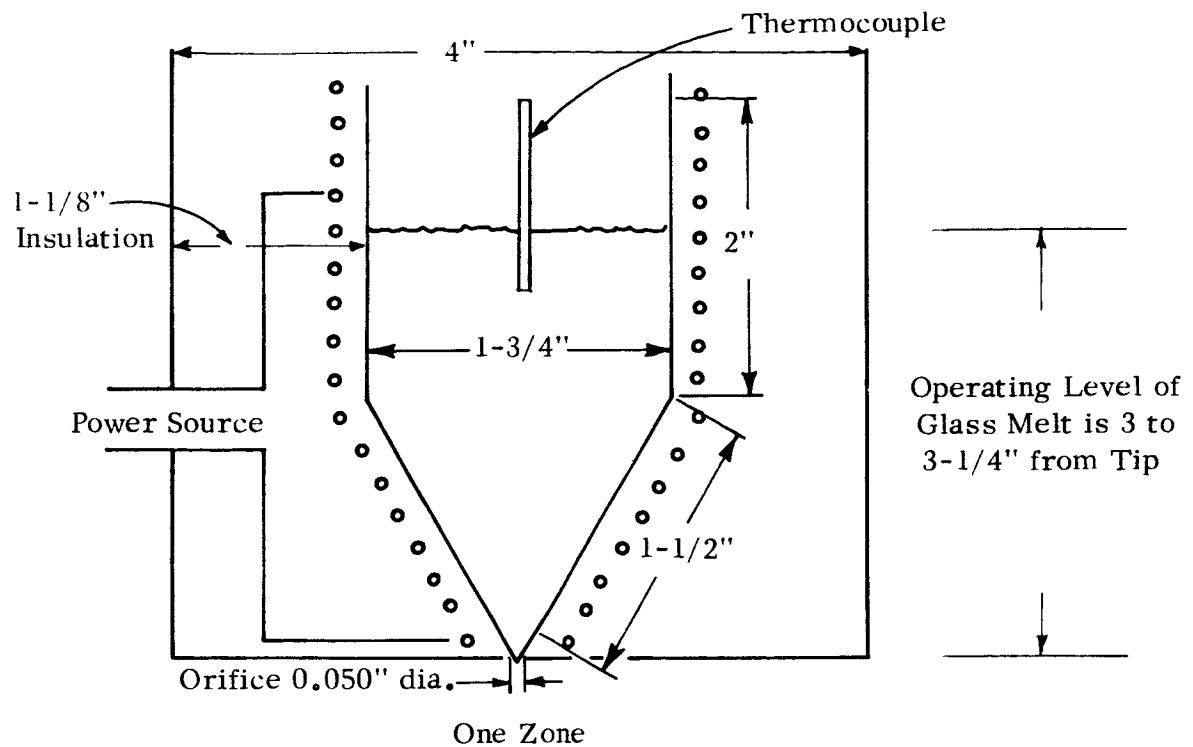
Two Zone

FIGURE 1   ONE- AND TWO-ZONE GLASS BUSHINGS
FOR GLASS MONOFILAMENT DRAWING

8
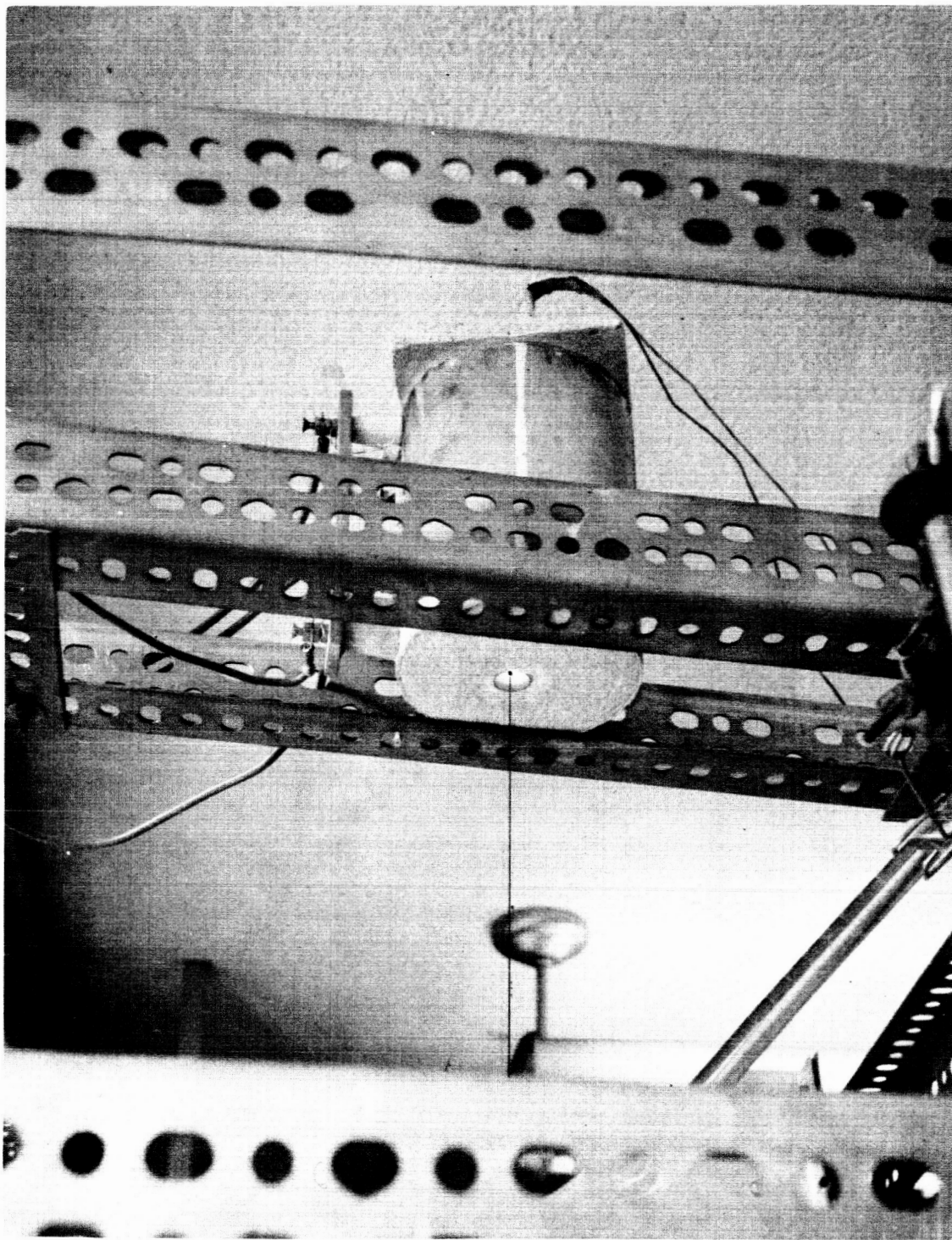
FIGURE 2   TWO-ZONE BUSHING IN OPERATION

use as a protective finish were not suitable to vapor application because of their high molecular weight (high vaporization temperatures) and subsequent degradation on heating. A burette fitted with a felt applicator (Figure 3) was finally selected for continuous application of both the finish and the resin.

The finish was applied to the glass, as it was drawn from the crucible, by a soft felt applicator which was maintained continuously wet by a controlled flow from the burette. The finish coated glass was dried by passing through a cylindrical heater adjusted to 90°C. The epoxy resin was finally applied employing the same basic burette and felt applicator techniques as used with the finish.

After the glass was tested for tensile on an Instron to assure that it had strengths averaging 400,000-500,000 psi, the filament was drawn onto a 5.75 inch diameter drum (Figure 4). The speed of the drum was measured by a stroboscope and adjusted to approximately 700 rpm, equivalent to a glass drawing speed of 1000 feet per minute.

The felt applicator was used to apply the finish to the glass mono-filament, and in a subsequent step the matrix resin was applied in the same manner, as illustrated in Figures 5 and 6. A Teflon guide attached to a reciprocating carriage was designed to give less than a 1° lead angle in the fabrication of the composite. The cylinder was cured and then cut into NOL rings for subsequent testing.

C. APPLICATION OF NICKEL FINISHES

An apparatus was designed that permitted continuous application of nickel from nickel carbonyl on glass monofilaments as part of the fiber drawing process. The facility consists of the following major components (Figure 7):

1. The nickel carbonyl supply and feed system

2. A hood enclosure (F) containing the "metal-coating chambers" (A, B, C)

3. The glass furnace

4. The resin applicator

5. The pressurizing system for chambers (A, C) which contains the carbonyl in the treatment chamber (B)

6. The split-tube furnace for heating the upper chamber (E)

7. The waste carbonyl combustion and exhaust system.

The nickel carbonyl is entrained as a vapor by means of carbon monoxide and passed into the center chamber (B) of the "metal-coating chambers" at a pressure of 1-1/2" to 2-1/2"(water). The upper and lower chambers (A, C) of the "metal-coating chambers" can be maintained at a pressure of about 6" water to minimize leakage of the carbon monoxide-carbonyl mixture. The chambers are isolated from ambient surroundings and separated from each other by means of graphite inserts (D) which have 2-mil diameter holes to allow passage of the monofilament. The glass furnace is about 15" above the upper chamber (A). A split circular heater (E) around this upper chamber (A) heats the argon contained therein. The carbonyl is exhausted through the middle chamber (B), and the entire assembly is enclosed in a well-ventilated hood.

The metal is coated by drawing the glass from the furnace through the "metal-coating chambers." Since the upper chamber is heated (550-580°F), the hot glass filament from the melt does not cool as rapidly as it would if exposed to ambient conditions. As the warm filament and hot gas interact in the plating chamber, the nickel carbonyl immediately decomposes and metallic nickel deposits on the warm glass surface. The coating chamber is kept cool to prevent deposition within the chamber and on its wall.

Detailed thermodynamic and kinetic data on the decomposition of nickel carbonyl are covered in a paper presented at the 95th Annual Meeting, American Institute of Mining, Metallurgical, and Petroleum Engineers, February 27 -- March 3, 1966, New York City.

11

Reciprocating
Carriage
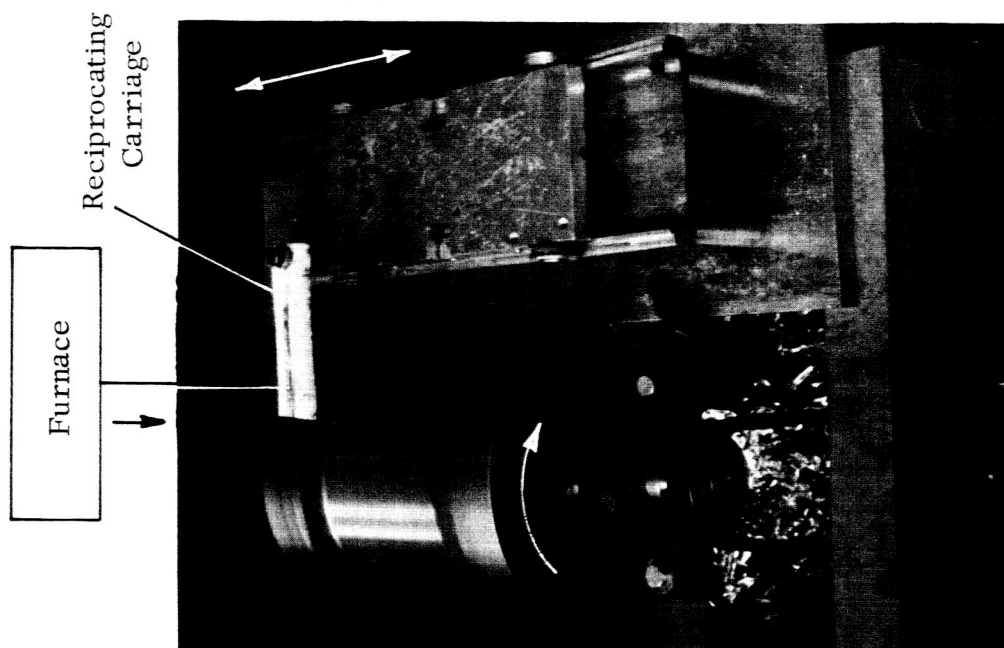
Furnace →

FIGURE 4   DRAWING DRUM

Burette

Felt
Applicator

Heating
Chamber
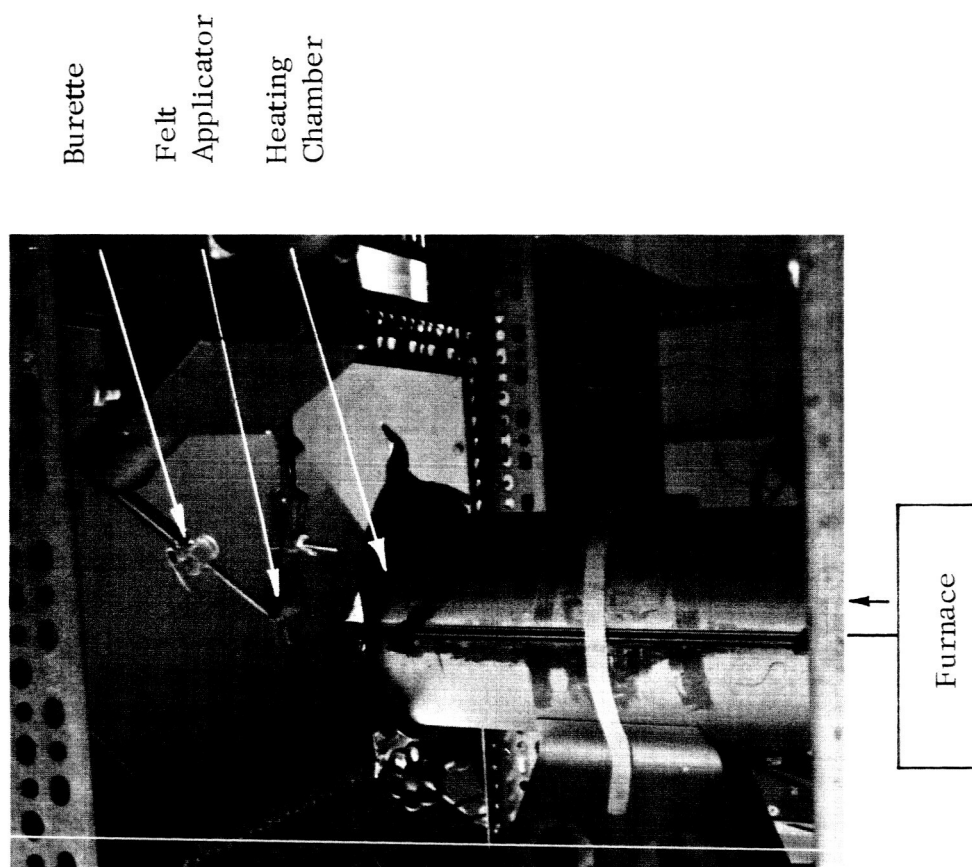
← Furnace

FIGURE 3   FINISH APPLICATION

12

FIGURE 6   COMPLETE ASSEMBLY, PILOT PLANT FOR APPLICATION OF ORGANIC AND NICKEL FINISHES

FIGURE 5   COMPLETE ASSEMBLY, LABORATORY FOR APPLICATION OF ORGANIC FINISHES

13
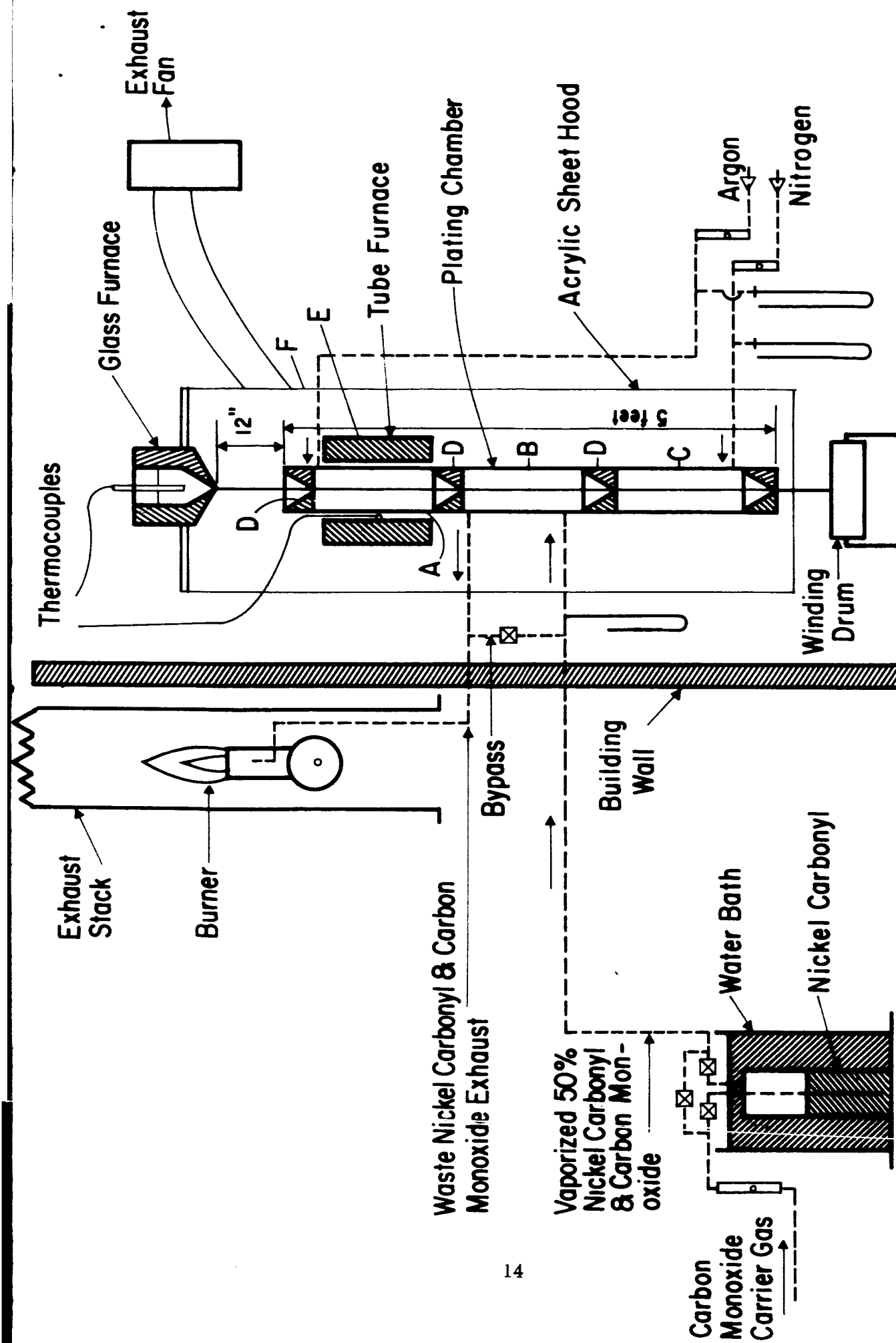
FIGURE 7   NICKEL CARBONYL COATING FACILITY

14

IV. SELECTION OF EXPERIMENTAL PROTECTIVE FINISHES

A. MATERIALS

On the basis of reported properties (as disclosed by literature search covered in the bibliography) the following materials were selected. Other materials were added during the progress of the work and are discussed in connection with the various screening tests.

1. Styrene-butadiene Silane Resins

At first, such a resin was prepared by the reaction of Buton-100 (styrene-butadiene-copolymer, molecular weight 8,000-10,000, Iodine No. of 300, Enjay Chemical Company) and trichlorosilane in the presence of 0.5% (by weight) of a peroxide catalyst. The silane adds across the double bond in the butadiene moiety to form $-CH_2-CH_2-Si-Cl_3$. The trichlorosilyl group hydrolyzes in methyl alcohol, and upon application to glass is presumed to react with the glass surface to form bonds that are moisture resistant; the organic portion of the resin has sufficient unsaturation to bond to the epoxy resin used as the composite matrix material:
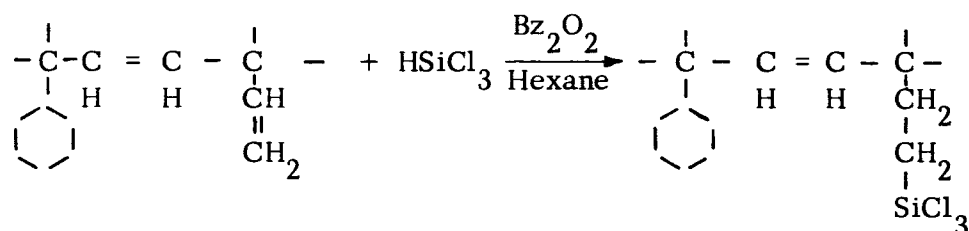
Since relatively large quantities of this material were required for test work, we obtained a commercially available analog in which the chlorine is replaced with alkoxy groups.* This compound, designated as Buton-silane, was supplied to us by Dr. Plueddemann of Dow Corning, and all test work was performed with this material.

This type of polymer was selected in the expectation that its flexibility would provide the extensibility and stress-absorbing properties of an elastomer and that its reactivity with glass would provide a good glass-to-epoxy interface.

---

*The alkoxy analog is similar to the chlorine compound in its reaction.

15

2. Fluorocarbon Silanes

The preparation of two fluorocarbon silanes was attempted, but only one was actually synthesized. The compound, $CF_3CF_2CF_2CH_2CH_2SiCl_3$, was intended as a model compound to determine whether the fluorocarbon portion of the molecule would repel water from the glass surface. The procedure used was that described in a paper by Geyer, et al.[1] A mixture of 30 gm of $CF_3CF_2CF_2CH = CH_2$ and 33.6 gm of $SiCl_3$ was sealed into a quartz tube and irradiated for 4 days, with shaking at room temperature, using a model 7420 Hanovia ultraviolet light. The tube was opened and the products were fractionated under vacuum. About 2 gm of product were obtained. It is believed that the poor yield is due to the decreased reactivity of the longer fluorocarbon chain compared to that of a shorter one. An attempt was made to prepare another fluorocarbon compound, $CF_3CF_2CF_2CH = CHSi(OMe)_3$, by the route shown below:

(a) $CF_3CF_2CF_2I + CH_2 = CHSiCl_3 \xrightarrow{\text{UV}} \overset{\text{(A)}}{CF_3CF_2CF_2CH_2CH(I)SiCl_3}$

(b) $A + MeOH \longrightarrow \overset{\text{(B)}}{CF_3CF_2CF_2CH_2CH(I)Si(OMe)_3}$

(c) $B + Quinoline \longrightarrow CF_3CF_2CF_2CH = CHSi(OMe)_3$
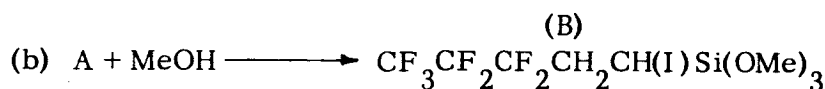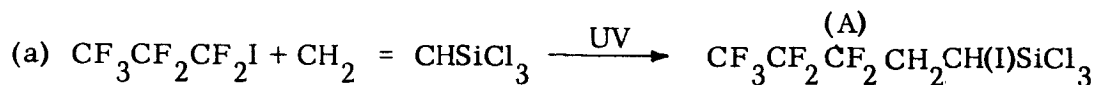
However, reaction (a) did not proceed satisfactorily and no further work was carried out on these silanes.

3. Hexachloroacetone

Hexachloroacetone was selected for screening because of its ability to react with hydroxyl groups on the glass and form a hemiacetal-active surface due to the presence of chlorine. Since ketones and aldehydes with high electronegative groups form dihydrols, reaction with the glass monofilament surface would be expected to be as follows:

$$\text{(glass-OH structure)} + xs\ (CCl_3)_2 C = O \longrightarrow \text{(cyclic product)} + (CCl_3)_2 C(OH)_2$$

---
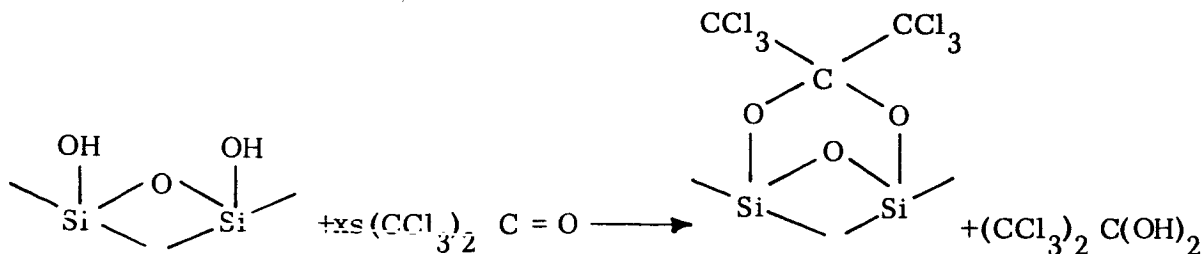
1. A.M. Geyer, R.N. Haszeldine, K. Leedham, and R.J. Marklow, "Polyfluoralkyl Compounds of Silicon," J. Chem. Soc., 1957, p.4472.

4. Silane Derivatives

Most silane derivatives are characterized by their excellent ability to wet glass and to provide a barrier against moisture. Therefore several of these materials were selected for screening, including a number of experimental and commercial silane derivatives supplied by Dow Corning, that were designed for use in glass-polyester resin composites.

      (a) 3-ethylamino - γ - aminopropyltrimethoxy silane
           (Dow Corning experimental resin)

      (b) glycidoxypropyltrimethoxy silane (Dow Corning Z-6040)

      (c) γ-aminopropyltriethoxy silane (Union Carbide A-1100)

      (d) trimethoxypropylaniline silane (Dow Corning experimental resin)

      (e) oxiron silane (Dow Corning experimental resin)

      (f) n-(trimethoxysilylpropyl) ethylenediamine (Dow Corning Z-6020)

      (g) β-carbethoxyethyltrimethoxy silane (Dow Corning experimental resin)

5. Polyamides by Interfacial Polymerization

The interfacial technique has been employed in applying certain types of polyamides to a continuous moving web. This reaction is a two-step process in which the filament is passed through an acylchloride solution and then through a diamine solution. The diamine condenses with the acylchloride to form a polyamide on the surface of the glass. However, it was found that the film formed was porous and adhered poorly to the glass, presumably because of solvent entrapment. The following reactions were evaluated:

a. Hexamethylenediamine was used in the first phase and adipyl chloride in perchloroethylene in the second. Clean glass slides were dipped into the solution and dried; the resultant film, as seen under the microscope, was very porous. It was found that fusing temperatures as high as 350°C eliminated the opaque appearance of the film but did not improve the porosity; therefore, this material was not tested further.

b. In a second interfacial polymerization, Dow Corning Z-6020 silane was reacted with an acyl chloride. However, again it was found that the film was extremely discontinuous, and further work with these materials was discontinued.

6. Urethane

Urethanes were included in the screening program because of their superior flexibility at low temperatures compared to most of the common polymeric materials being considered. Toluene diisocyanate and epichlorohydrin-glycerine were mixed in a 1:1 molar ratio at room temperature in carbon tetrachloride to form the basic prepolymer which was applied to the glass and evaluated as a typical finish.

7. Metal Carbonyls

The approach to metal coating was based upon the use of metal carbonyls that decompose at low temperature (50-100°C) in order to avoid the possibility of damaging the glass filament by exposing it to high temperature. Furthermore, the glass drawing rates being considered were in the order of 300-1000 ft/min; at these speeds it would be difficult for the glass to reach temperatures of 300-500°C without employing a much more elaborate setup than initially planned.

Two chromium compounds were screened: Chromium carbonyl $(Cr(CO)_6$, K & K Laboratories, Inc.) and bis-(methylcyclopentadienyl) chromium (AS-33K, Union Carbide Corporation). However, these decompose at 300-500°C, and since they would have entailed a more elaborate setup, they were eliminated from further consideration. In their place nickel carbonyl (which has a decomposition temperature of 40°C) was selected as a model system.

A simple procedure was used to determine if the metal could be decomposed on heated glass and produce an acceptable bond. Ten-mil-diameter glass specimens were positioned on a brass rod which was used as the heat sink and inserted in a glass tube two feet long. The rod was heated by a tube furnace, and a thermocouple embedded in the metal rod was used to measure the temperature.

The metal was plated on the glass by first evacuating the tube and then raising the temperature of the heat sink to the decomposition temperature of the metal carbonyl. The metal carbonyl was then allowed to enter through a regulating valve from a storage tank. The quality of these coatings, however, was unsatisfactory for adhesion tests, probably because of contamination. Theoretically, the nickel carbonyl should provide the necessary metal-to-glass adhesion. Therefore, in order to eliminate any possible contamination, further evaluation was performed by applying the metal (through nickel carbonyl) directly on the glass during the drawing operation.

18

8. Epoxies

Several modified epoxies were also evaluated as potential protective finishes, so as to take advantage of the abrasion resistance provided for the glass fibers, and at the same time provide a finish that would be compatible with the epoxy matrix binder. Ciba's Araldite 6005, with and without Araldites RD-1 (butyl glycidyl ether) and RD-2 (butane-diol diglycidyl ether), was used as a matrix material or admixture to the finishes.

B. SCREENING OF FINISHES

The materials selected as potential protective coatings for glass were screened for their ability to wet out the glass, adhere to the glass, and resist moisture. The following tests were used to characterize these materials:

1. Adhesion

After considering several tests for determining the adhesion of treated glass to an epoxy resin matrix, a method developed in the MIT Plastics Laboratory[1] was selected. In this method, adhesion is determined from the measurement of the resistance of the resin-glass bond to an interfacial tension. (See Figures 8 and 9.) Ten-mil coated glass rods were embedded in epoxy resin (System B, Section V, Page 38) along the longitudinal axis of the test specimen and cured at room temperature to minimize stresses due to exotherm and shrinkage. The specimens were then loaded in compression. A tensile stress normal to the resin-glass interface is created when the sample is compressed because of the greater Poisson's ratio of the resin. The bond failing point, or loss in adhesion, between the fiber and the resin is detected by the appearance of a light streak along the fiber if it occurs before total failure of the specimen ("ultimate compressive failure").

Failure of the resin-glass bond may be caused by applying either a shear stress along the length of the fiber or a tension normal to the glass-resin interface. Ideally, these two effects should be separated so that failure will take place by either the shear or the radial stress, but not both. The test specimen used in this work was designed to eliminate the shear effect and to cause failure by radial stress at the interface. If the mode of failure is known, the theoretical expression for bond stress, in terms of the axial load on the specimen, can be applied.

---

1. L. J. Broutman, "Resin-Glass Bond Studies," MIT Project 8225-14, June 1960.

Compression
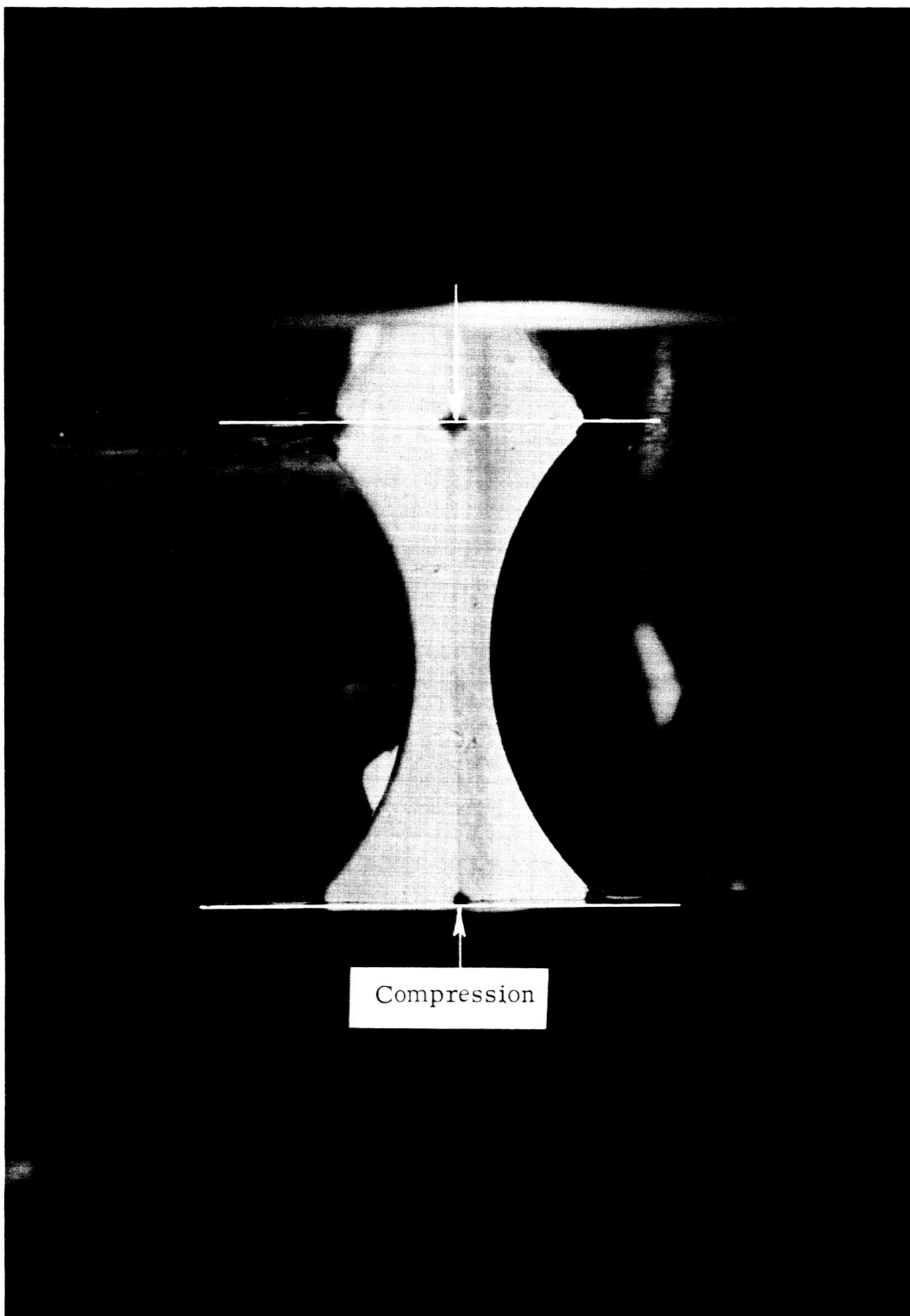
FIGURE 8   CURVED NECK SPECIMEN DURING ADHESION TEST
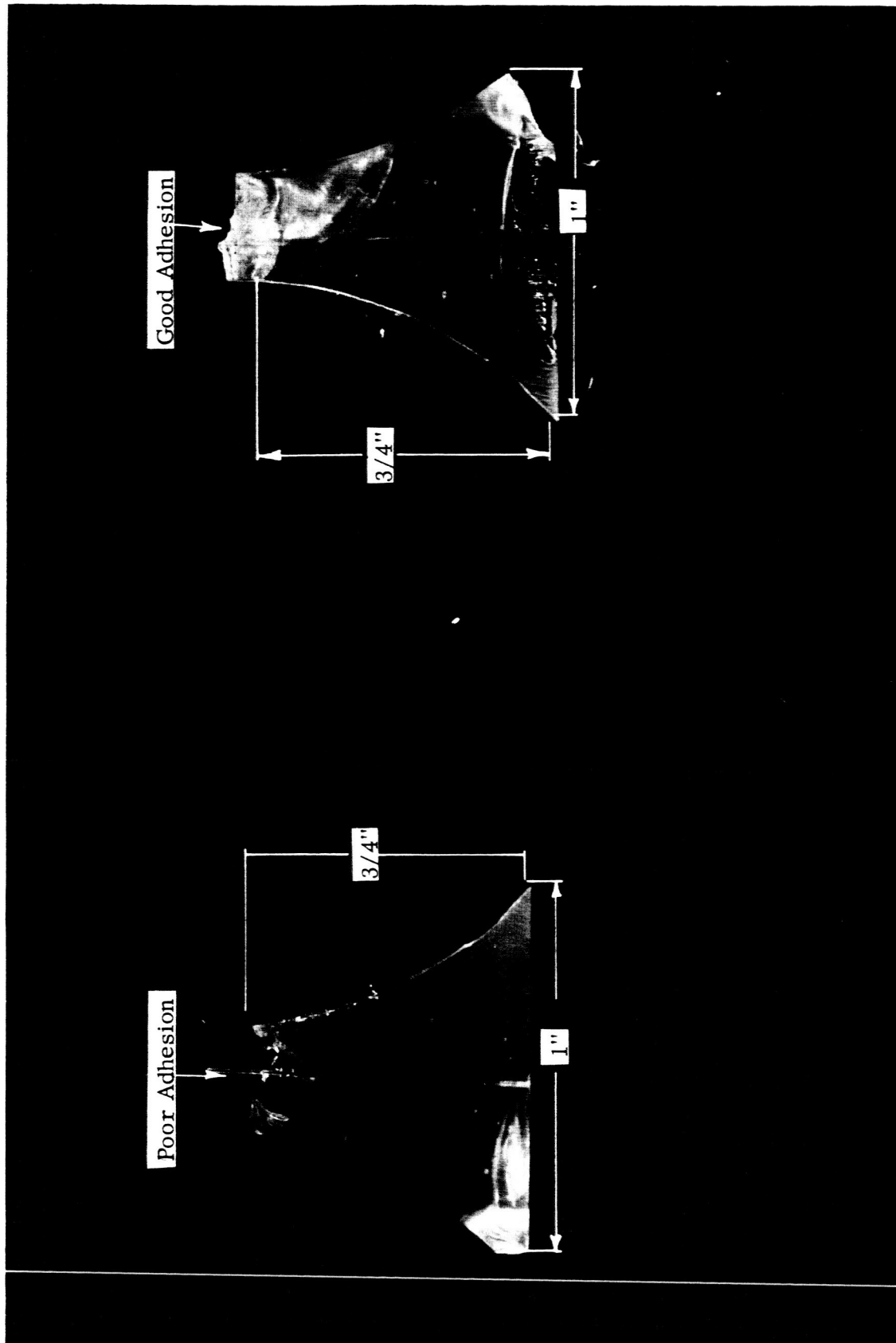
FIGURE 9   CURVED NECK SPECIMENS AFTER ADHESION TEST

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Table 1 lists a number of different coatings applied to glass monofilaments and shows that a material which adheres poorly--such as silicone R-671, commonly used as a release agent--debonds at a low debonding strength (7,400 psi) prior to specimen failure.

The two tests with Araldite 6005 (10% triethylene tetramine as a curing agent) show that this epoxy, believed to be more or less equivalent to that used in HTS finishes, bonds well with glass. However, if such an epoxy finish is cured prior to being embedded in the matrix, the bond appears to be somewhat weakened (Table 1, Tests 2 and 3). The only other finish in this series showing no debonding prior to sample failure was the Dow Corning Buton-Silane (Table 1, Test 4). The urethane formulation (prepared in the ADL laboratories) (Table 1, Test 5) and a mixture of the Araldite 6005 with an organic ammonium silicate (Table 1, Test 6) debonded during specimen failure. The organic ammonium silicate is of interest, since it can be applied from aqueous solution and still yields a tight bond and a reasonably water-resistant finish. The two typical finish materials (Table 1, Tests 6 and 8) showed only mediocre adherence in this test.

In addition, Union Carbide A-1100 (aminopropylsilane) and the amine-cured Araldite 6005 were tested before and after a 24-hour boil (Table 2). The Araldite 6005 finish (cured prior to embedding) bonded rather poorly, in contrast to the reasonable bond obtained with a similarly cured finish, as shown in Table 1. Neither sample showed any evidence of a decrease in bond strength after a 24-hour boil.

2. Wetting

The requirement for good wetting at the matrix-finish-glass interfaces is generally recognized. Water repellance is also generally accepted as a desirable feature for finishes. Although there is some disagreement about how important wetting is to the strength of resin-glass fiber composites, reasonable wetting properties certainly minimize porosity and voids fabrication and improve the water repellancy of finish-coated fiberglass during storage.

Static contact angle tests (Table 3) were used to screen Nylon 6-6 and various silicon-organic compounds as to proper combination of water repellancy and wetting by Epon 828 and catalyst CL. The Epon 828 is essentially equivalent to the Araldite 6005 resin system used in other tests. The finishes were applied to glass slides and the wetting angle determined by measuring an enlarged projection of a drop of water or of Epon 828, respectively.

22

TABLE 1

CURVED NECK SPECIMEN

ADHESION TEST DATA

Finish	Debonding Stress (psi)	Remarks
1. Dow Corning R-671	7,400	Partially debonded prior to test.
2. Ciba Araldite 6005 Resin (10% Triethylene tetramine)	No Debonding	Finish was not cured prior to embedding in specimen.
3. Same as No. 2	18,000	Finish oven-cured for one hour at 100°C prior to embedding.
4. Dow Corning Buton-Silane	No Debonding	
5. Urethane (ADL Prepn)	18,000	Partially debonded.
6. Dow Corning Z-6020 (n-Trimethoxysilylpropyl ethylenediamine)	15,700	Some debonded areas prior to testing.
7. Ciba Araldite 6005 with 20% organic ammonium silicate II 6 (Philadelphia Quartz Co.) 20 pts.	18,000	
8. Dow Corning Oxiron Silane	10,000	

Note: All specimens were embedded in a matrix consisting of 100 parts ARALDITE 6005 and 10 parts TRIETHYLENE TETRAMINE and cured at room temperature. Ultimate compressive failure of the specimens occurred at about 18,000 psi. Where no debonding stress is noted, bond was unaffected at specimen failure. The debonding stress data is based on an average of 10 individual determinations.

TABLE 2

CURVED NECK SPECIMEN

ADHESION TEST DATA

(BEFORE AND AFTER 24-HOUR BOIL)

Finish	Debonding Stress (psi)		Ultimate Compressive Strength (psi)	
	"Dry"	After Boil	"Dry"	After Boil
Union Carbide A-1100 (Y-aminopropylsilane)	16,300	**	17,000	12,000
Araldite 6005* 10% triethylene- tetramine	11,000	11,000	17,000	12,000

Note: Embedded as in Table 1.

*Finish cured prior to embedding

**Boiled A-1100 did not debond on failure

TABLE 3

STATIC CONTACT ANGLE TEST DATA
(On Glass Slides)

| Coating | Contact Angle (degrees) | | | |
| | Water | | Epon 828 & CL Catalyst | |
	5 sec	30 sec	5 sec	30 sec
1. Nylon 6-6 (10% Solution in Methyl Alcohol)	33	27	17	15
2. Υ-Carbethoxyethyl-trimethoxy silane	35	31	39	36
3. 3-Ethylamino-Υ-aminopropyltrimethoxy silane	72	67	20	26
4. Glycidoxypropyl-trimethoxy silane (Dow Corning Z-6040)	56	50	26	23
5. Dow Buton-Silane	82	69	44	37
6. Υ-Aminopropyltriethoxy silane (Union Carbide A-1100)	49	44	32	34
7. Trimethoxypropyl-aniline silane	49	44	32	34
8. Control (No Coating)	24	18	formed droplets	

Inspection of Table 3 shows that Dow Buton-Silane and 3-ethylamino-Y-aminopropyltrimethoxy silane have the highest water repellancy. Although Buton-silane has the highest contact angle with Epon 828, it still can be considered as having adequate wetting characteristics.

For possible admixture with finishes, epoxies Araldite 6005 and E-289, and the reactive additives Araldite RD-1 and RD-2 (the latter also in admixture with Araldite 6005) were tested for their ability to wet glass. Static and dynamic wetting were determined by using the apparatus shown schematically in Figure 10. Figures 11a and 11b are representative photographs of the angular measurements. Ten-mil glass rods were used in these tests. As can be seen from Table 4, Epon 289 appears to be equal to Araldite 6005 and both wet poorly under dynamic conditions. Both Araldite RD-1 and RD-2 appear to wet well, Araldite RD-2 particularly under dynamic conditions. As can be seen, 10% addition of Araldite RD-2 substantially improves the dynamic wetting conditions of Araldite 6005. (A similar effect would be expected with such diluents when added to Epon 828.)

A further brief series of tests, with 5- and 30-second static and advancing and receding dynamic contact angle measurements was made as shown in Table 5. Pretreatment with hexachloracetone, as expected, gave good wetting properties. The Araldite 6005, amine cured and silane modified matrix material gave rather poor wetting.

3. Photoelastic Stress Observations

A brief review of the stress considerations, originally developed by Matta and Outwater,[1] led to the consideration of the "resin enclosed by glass concept." Various finishes were therefore coated around the inside of glass cylinders, epoxy resin was then cast inside the coated cylinders and the photoelastic stress patterns that were found were observed. As can be seen from Figures 12 and 13, complex stresses were built up in the samples using a conventional finish (amino silane) at the resin-glass interface or an epoxy without a finish. In the sample having a silicone release agent at the resin-glass interface, the resin and glass acted as independent systems.

On boiling (24 hours) the epoxy resins swelled considerably. However, even though the glass cylinders were completely shattered due to the swelling of the resins in all instances, it appears that the final stress patterns obtained in the samples without the release agent were influenced by the conditions at the interface. We believe, however, that observations obtained in this manner are highly idealized and that detailed study of various interface systems would not be worthwhile in the context of this program.

1. J.A. Matta and J.O. Outwater, "The Nature, Origin, and Effects of Internal Stress as in Reinforced Plastic Laminates," SPE TRANS., Vol.4, No.2, April 1964, p. 120.
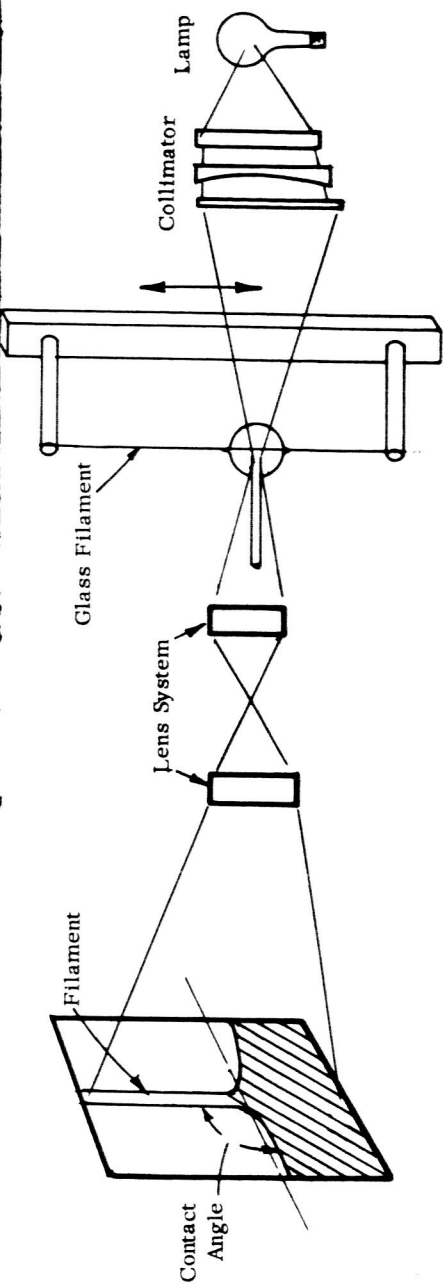
FIGURE 10   SCHEMATIC DIAGRAM, WETTING ANGLE APPARATUS
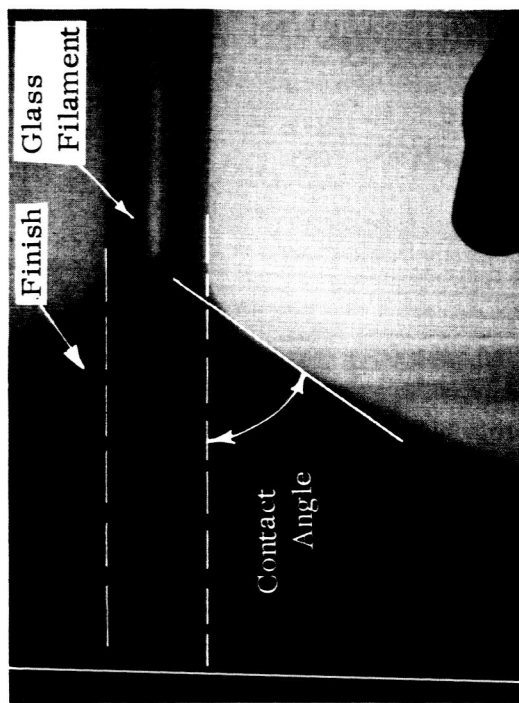
Glass: Epoxy-Silane Finished
Resin: 6005 and RD2
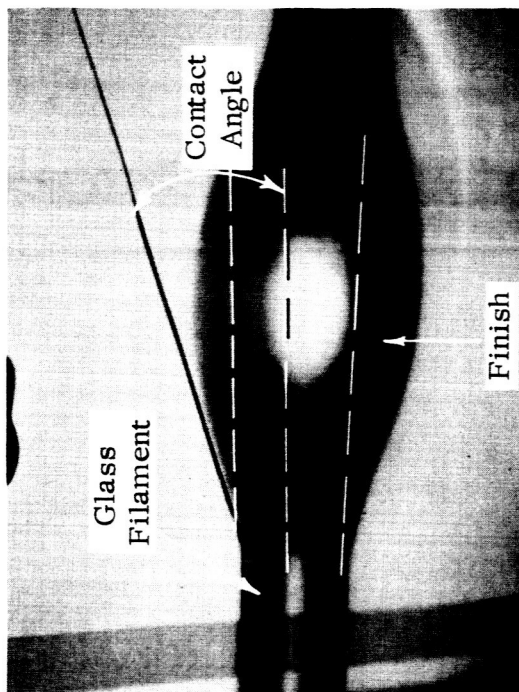
Glass: HCA Finished
Resin: 6005 and RD2

FIGURE 11   WETTING ANGLE PHOTOGRAPHS

27

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TABLE 4

CONTACT ANGLE TEST DATA OF EPOXY RESINS ON UNTREATED
10-MIL GLASS RODS

Resin	Static Contact Angle[a] (Degrees)	Dynamic Contact Angle[b] (Degrees) Advancing
Araldite 6005	34	Poor wetting, droplet formation
Araldite RD-1 (butyl glycidyl ether)	26	30
Araldite RD-2 (butane diol diglycidyl ether)	27	19
Union Carbide E-289 (cyclo aliphatic epoxide)	40	Poor wetting, droplet formation
Araldite 6005 Araldite RD-2 (10% by weight)	30	32

(a) one-minute droplet formation

(b) 5-ft/min glass velocity

TABLE 5

CONTACT ANGLE TEST DATA ON TREATED 10-MIL GLASS RODS

Finish	Static Contact Angle (Degrees)		Dynamic Contact Angle (Degrees) 5 ft/min	
	5 Sec	30 Sec	Advancing	Receding
Hexachloroacetone	22	24	30	34
Araldite 6005 10% triethylenetetramine 10% γ-aminopropylsilane	52	32	50	36
Untreated Control	34	30	79	32

Note: The rods were coated with the designated finish and dried, then a mixture of Araldite 6005 and Araldite RD-2 was used to measure the contact angles both by static and dynamic methods.

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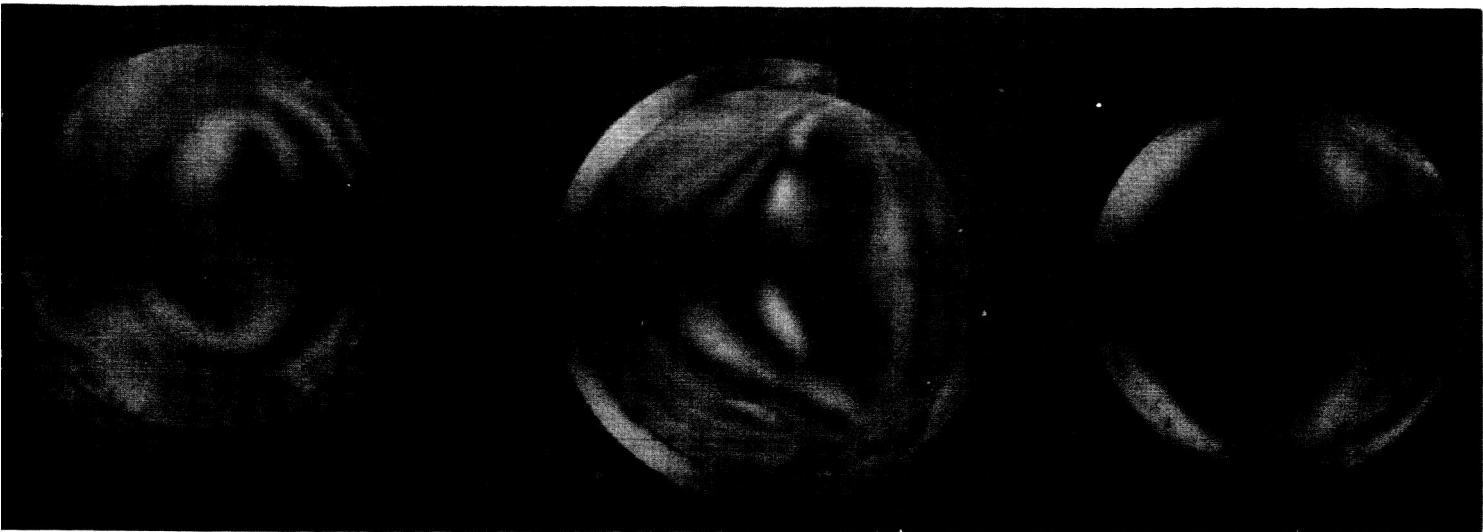
FIGURE 12   PHOTOELASTIC STRESS ANALYSIS OF
EPOXY-FILLED HOOPS

FIGURE 13   PHOTOELASTIC STRESS ANALYSIS OF EPOXY-FILLED
HOOPS, AFTER BOILING WATER EXPOSURE

30

4. Flexural Strength

These tests were made to determine the compatibility of the urethane (see Section IV A.6 Page 18) finish with the Araldite 6005/catalyst CL system, as well as with the properties of the urethane resin as such.

Two flat, parallel-oriented, filament-wound panels were fabricated from urethane-coated, single-end E-glass (204 filament) roving. One panel was prepared with the conventional Araldite 6005/catalyst CL resin system. The other panel was impregnated with the same experimental urethane resin previously used as the finish material.

Flexural specimens were prepared and tests performed at room temperature and at -320°F. As expected, the urethane matrix samples had a higher strength at -320°F than at room temperature, as shown in Table 6.

TABLE 6

FLEXURAL STRENGTH TEST OF URETHANE-COATED GLASS FILAMENT-WOUND COMPOSITE

Resin Matrix	Resin Content (%)	Room Temp.	-320°F
Araldite 6005 (100 Parts) Triethylenetetramine (10 parts)	18	13,400 psi	8,950 psi
Urethane (Experimental)	15	7,200 psi	9,800 psi

Note: The data is based on an average of five individual determinations.

31

The value of 13,400 psi for the urethane/epoxy/CL composite agrees with reported data for standard and HTS epoxy filament composites[1] and it was concluded that the urethane is compatible with the epoxy resin.

5. Monofilament Tensile Strengths

To insure that glass filaments acceptable for composite structures were produced in the glass-drawing operations, samples were taken and conditioned as discussed below.

The tensile strength was determined with a table model Instron Universal Testing Machine with an Instron A cell. The A cell has a range of 0 to 50 gms, and a sensitivity of 0.5 gm (Figure 14). The monofilament was collected and transferred to the testing tabs by covering the forks with double-sided masking tape for attachment of the filaments. Double-sided tape was placed on part of the testing tabs and the filament transferred by laying the tab on the fork so that the exposed tape on the tabs was within the fork (Figures 15a,b,c). The filament was then cut free and tested for fiber diameter and strength. The fiber diameter ranged from 10-15 microns; however, after establishing the optimum melt and tip temperatures and drawing speed (as discussed in Section III A), 10-12 micron monofilament was obtained over a six-hour run.

The diameter of organic-coated filaments was measured by an Insco Vibroscope (Figure 16); the Vibroscope determines the harmonic frequency of the filament and the diameter is calculated from this according to the following formulas:

$$dc = \frac{2.205 \times 10^8 \, g}{f^2 l^2}$$

where:

$\quad dc$ = fiber denier

$\quad g$ = tension weight (grams)

$\quad f^2$ = frequency (cps squared)

$\quad l^2$ = fiber length (squared)

$$D = 7.2 \times 10^3 \left(\frac{denier}{density} \right)^{1/2}$$

where D = equivalent diameter (mm)

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1. B. W. Shaffer, "Material Properties of Reinforced Plastics," SPE Trans., Vol. 2, No. 4, Oct. 1962, p. 362.
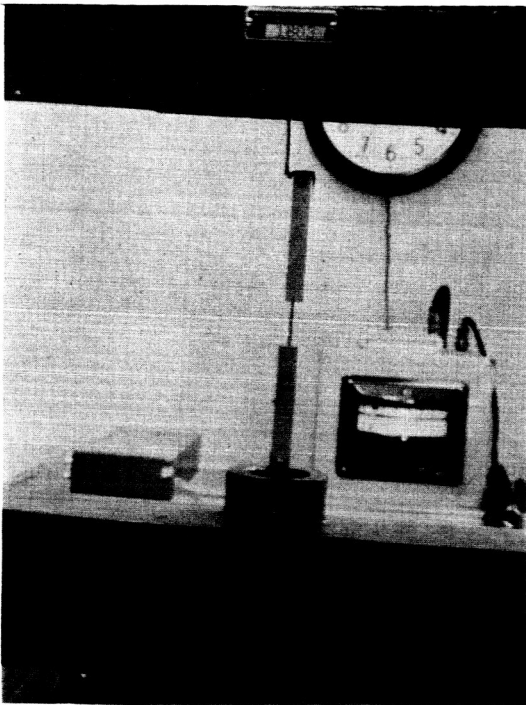
FIGURE 14   INSTRON TENSILE
            MACHINE WITH TABS
            FOR TESTING
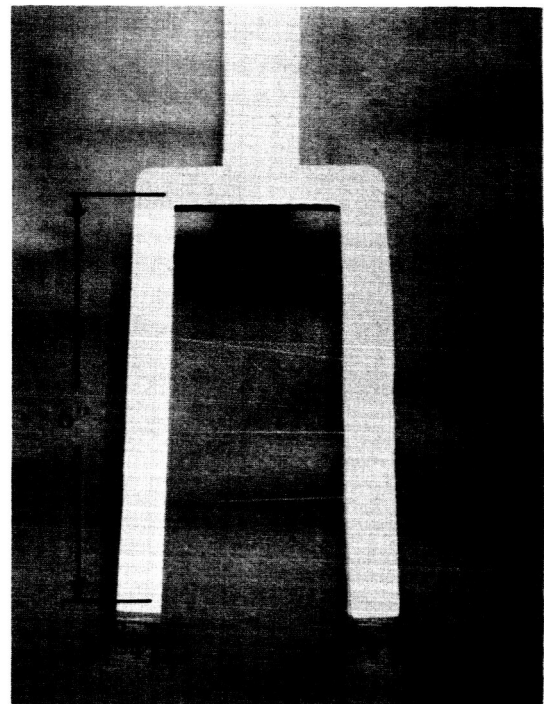
FIGURE 15a
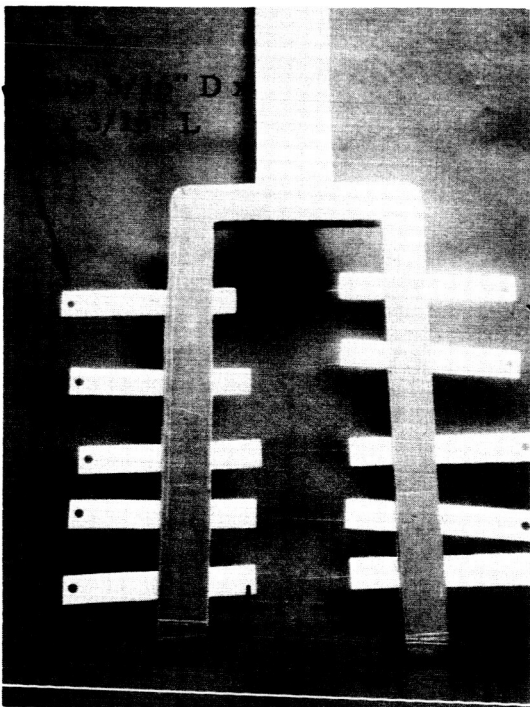
FIGURE 15b
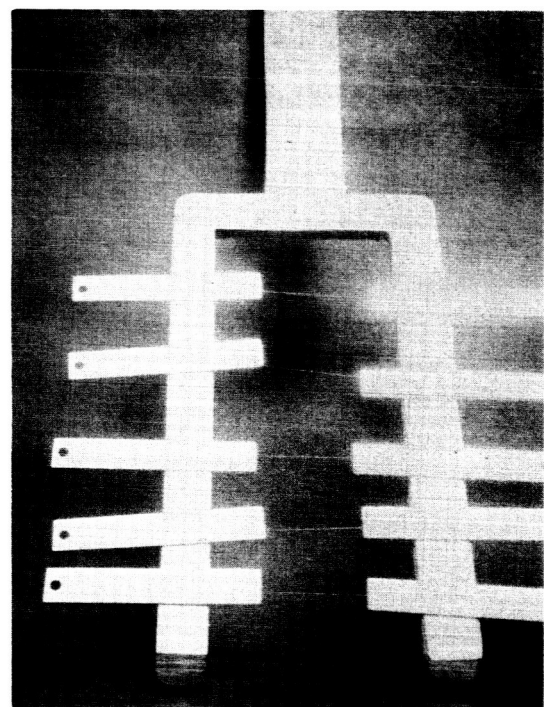
FIGURE 15c

FIGURE 15a, b, c   MOUNTING FORKS AND TABS

Sample is Mounted Here
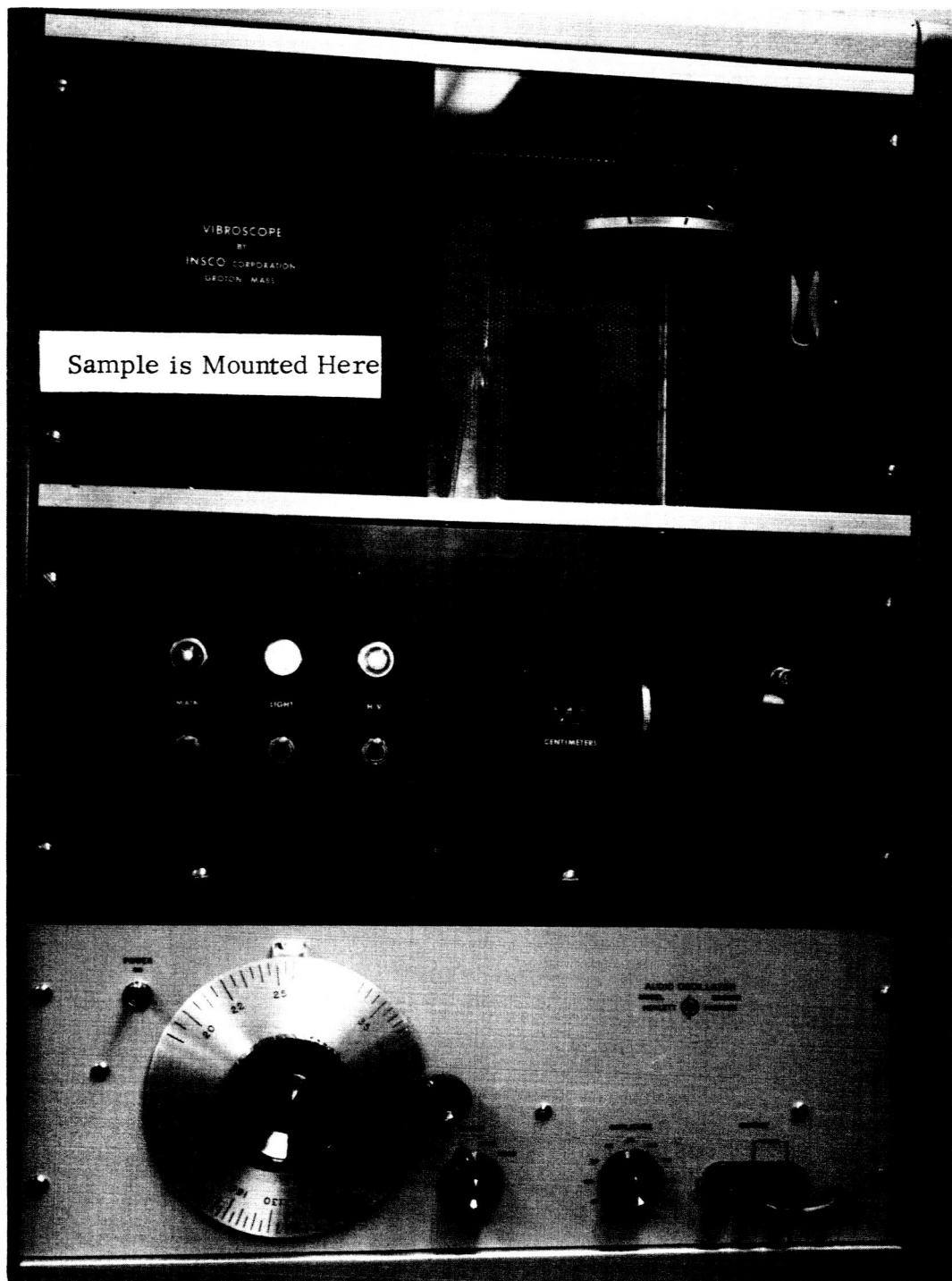
FIGURE 16   VIBROSCOPE

The metal-coated filaments would not vibrate and therefore could not be tested in the Insco Vibroscope. Therefore, the diameters of metal-coated filaments were measured by means of an optical microscope and a calibrated micrometer grid. Comparative tests for filament thickness, using a microscope in one case and the Vibroscope in the other, indicated no change in the tensile strengths; therefore it was concluded that the vibration of the filament in the Vibroscope did not affect the tensile strength of the glass.

The findings are shown with samples aged at 50% R.H. and 77°F (Table 7). Each test was based on 20 specimens and an average range is reported. These results are in good agreement with those of Cameron,[1] who reported that the strength of the E-glass fibers does not alter appreciably between 19 and 95 days' exposure to laboratory air at 32-44% R.H., the major decrease in strength having occurred in the first 19 days of aging. The maximum strength decrease reported by Cameron is between 9 and 10%.

In order to determine the effect of the more promising coatings, small quantities of 10-micron glass filaments were coated during the drawing operation with: (1) Buton-silane finish, (2) urethane finish, and (3) nickel (2.33% by weight). The urethane-coated fibers could not be tested successfully, since the coating caused slippage in the jaws. The tests, made on all finished filament (Buton-silane, urethane, and nickel) and control (uncoated filament), show no pronounced aging tendency for either coated or uncoated filaments. The high values for the Buton-silane (Dow) finished samples are not fully understood, but possibly they are due to the use of a superior fiber lot.

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1. N.M. Cameron, "An Investigation into the Effect of Environmental Treatment on the Strength of E-Glass Fibers," TAM Report (Univ. of Illinois) No. 274, Jan. 1965.

TABLE 7

"E"-GLASS MONOFILAMENT-AGING TEST RESULTS

	Days Exposed to 50% R.H. at 77°F	Tensile Strength (psi)	Range (psi)
A. Uncoated Monofilament			
	0	388,000	65,000
	1	412,500	45,000
	5	420,000	45,000
	30	378,000	50,000
	Average	399,622	
B. Buton-Silane Finish			
	0	665,000	85,000
	1	605,000	70,000
	5	640,000	70,000
	30	570,000	150,000
	Average	620,000	
C. Nickel Finish			
	0	384,000	40,000
	7	380,000	45,000
	30	379,000	48,000
	Average	381,000	

D. Urethane Finish

No tensiles could be obtained with the urethane finish, since the coated filament continuously slipped in the tensile tabs.

Note: The filament used in all our studies averaged 10-12 microns in diameter.

36

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V. RESIN MATRIX EVALUATIONS

To facilitate the method of resin application the viscosity of the standard Ciba Araldite 6005-catalyst CL epoxy system was reduced with a reactive diluent, Ciba's Araldite RD-2 (1,4-butanediol diglycidyl ether).

To determine the effects of the Araldite RD-2 diluent on the resin and composite mechanical properties, two formulations were cast and cured (2 hrs at 85°C, 4 hrs at 150°C) as films 20 mils thick on paper. These films were tested to determine their ultimate tensile strength and elongation (Table 8).

TABLE 8

STRENGTH AND ELONGATION TEST RESULTS[a] FOR RESIN WITH AND WITHOUT DILUENT
(20-mil Films)

Resin System[b]	Ultimate Tensile Strength (psi)	Ultimate Elongation (%)
A: Araldite 6005, 100 parts Curing Agent CL, 14 parts	5,200	4.0
B: Araldite 6005, 100 parts Curing Agent CL, 15 parts Araldite RD-2, 5 parts	2,020	3.5

a. The average tensile strength and elongation were obtained from five individual test specimens.

b. Curing cycle: 2 hours at 85°C, 4 hours at 150°C.

The substantially different strengths of these two resin systems, as measured in this test, were not apparent in the overall properties of NOL rings fabricated from these resins. Possibly, the similarity of the ultimate elongations (4.0 and 3.5) may account for the retention of the composite strengths of the filament-wound composites.

37

In addition, NOL rings were wound using resin systems A and B with 20-end E-HTS roving supplied by Owens-Corning Fiberglas. Two sets of rings were prepared--at 0.10-pound per end and 0.25-pound per end tensioning, respectively--and tested. Resin system B, because of its lower viscosity, was easier to coat onto the glass monofilament.

Rings made from roving were fabricated as shown in Table 9 with tensioning of 0.10 and 0.25 pound per end, respectively. The poorer workability of the unmodified resin is evidenced by the much higher void content that results with the higher tensioning. The modified resin exhibited lower viscosity as observed by visual examination. No viscosity data, however, was obtained on the two compositions.

TABLE 9

COMPOSITE TENSILE STRENGTH TEST RESULTS ON NOL RINGS WOUND WITH THE STANDARD AND MODIFIED RESINS
(Average of five samples)

Resin System	Tensioning (lb/end)	Composite Strength (ksi)	% Resin by Wt	% Voids by Vol.	Glass Stress (ksi)
A	0.1	137	35	4.9	268
B	0.1	177	32	1.8	358
A	0.25	236	17	11.4	340
B	0.25	178	25	2.6	310

Because of the large variation in resin content, glass stress was calculated for comparison purposes. (Glass stress is defined as the composite strength divided by the glass volume.) It is evident from Table 9 that no significant differences in tensile strength can be attributed to the use of RD-2 as a diluent.

The effect of water on the modified epoxy resin was examined by boiling the NOL ring samples for two hours; the test results are shown in Table 10. Again, no significant difference in tensile strength retention after a two-hour boil was observed, and the RD-2 modified epoxy resin, therefore, was used for composite ring tests.

TABLE 10

EFFECT OF WATER ON THE COMPOSITE TENSILE STRENGTH OF HTS-ROVING COMPOSITES

Resin System	Resin Content (%)	Dry (ksi)	Composite Strength 2-hr Boil (ksi)	Retention (%)
A (No RD-2 Diluent)	35	137	132	96
	17	236	190	94
B (With RD-2 Diluent)	32	177	164	93
	25	178	164	93

Further tests using 5" x 1/2" x 1/4" test bars (prepared from cast resin) to examine the water resistance of matrix materials are shown in Figure 17. Both aromatic and aliphatic amine-cured epoxy deteriorate when exposed to moisture.

The aliphatic amine system (6005-TETA), which cures at room temperature, was evaluated for both the moisture and temperature effect of immersion in 190°F water. Figure 17b shows that at least an additional 15% strength deterioration is due to the moisture exposure.

Interpretation of Figure 17a is complicated by an apparent annealing of the bars during the drying cycle which resulted in a higher initial strength. It is apparent, however, that the moisture exposure has caused permanent deterioration.
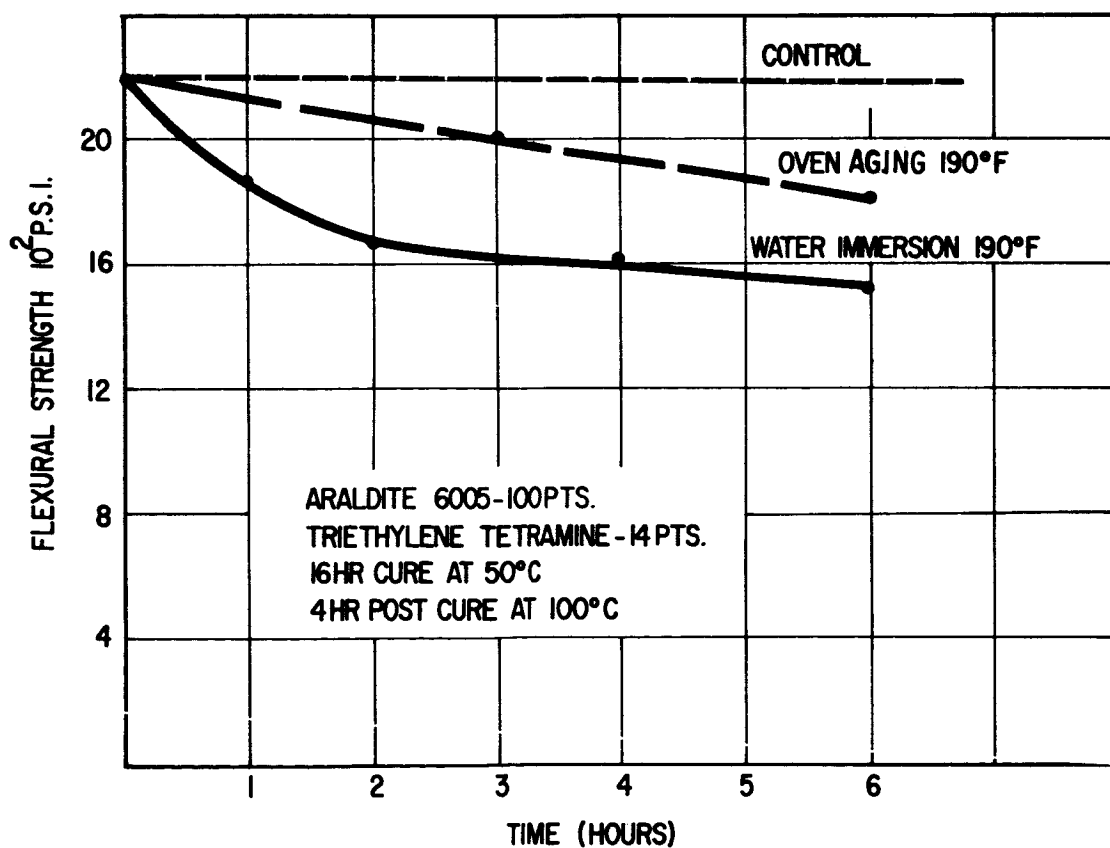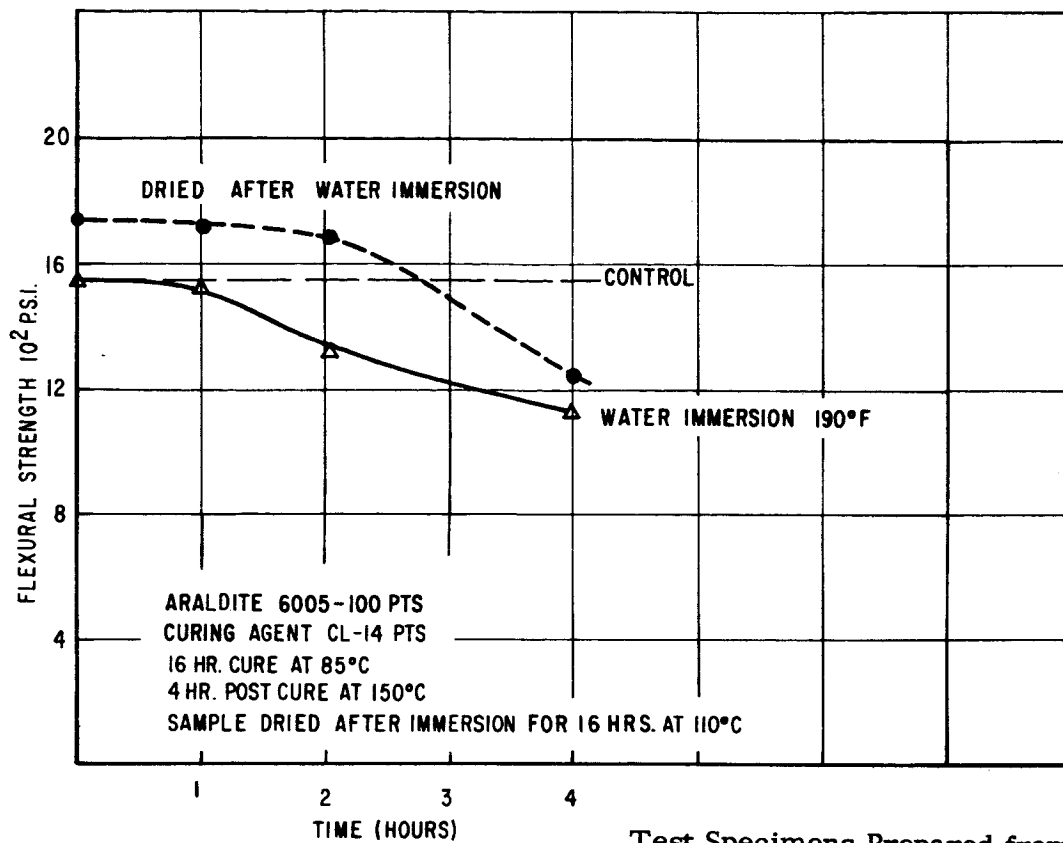
FIGURE 17   EPOXY RESIN ACCELERATED ENVIRONMENT TEST

VI. FABRICATION AND TESTING OF ORGANIC-COATED GLASS MONOFILAMENT-WOUND NOL RINGS

The most promising organic protective finishes of those screened were Buton-silane and urethane. (See Section IVA.) Therefore, the glass mono-filaments were coated directly during the glass drawing operation with these finishes and with the matrix resin (Araldite 6005, 100 parts; Araldite RD-2, 5 parts; Curing Agent CL, 14 parts) and NOL rings fabricated as follows:

The glass was drawn at a rate of 800-1000 ft/min as measured by a stroboscope on the winding drum. The glass was coated with the organic finish by means of a felt applicator and the coated glass then passed through a tube furnace to dry the organic finish. The glass then passed over a second felt applicator which applied the epoxy resin binder. The glass filament next passed through a Teflon guide attached to a reciprocating carriage which was designed to give less than a 1° lead angle. The filament was finally wound on a 5.75-inch diameter drum and in this manner a 4.75-inch cylinder was obtained, which after curing at 85°C for four hours and 125°C for two hours, was removed. The surface of the cylinder was finished off (smoothed) with a machine tool and then sectioned into individual rings 0.375-inch wide. The normal or specified specimen is stated to be 0.125 ± 0.603-inch thick, prepared in a close mold. Dimensions of specimens in this program were from 0.025 to 0.040 inch thick and 0.375 inch wide. The tests performed on these rings are described in the following sections.

A. FLEXURAL STRENGTH OF NOL RING SEGMENTS

Flexural strength has been used frequently to evaluate the adhesive strength between reinforcement and resin matrix, and was therefore tried as a method of evaluating the composite structure. ASTM D790-59T test for determining the flexural properties of the composites specifies a composite thickness of not less than thirty mils. However, at this thickness there was considerable buckling of the test specimens. Values of the NOL ring segments are shown in Table 11 for specimens which were reasonably nondeformed.

It was therefore decided that tensile strength tests would be used as the major evaluation tool during most of the program. Subsequently the inter-laminar shear strength test on NOL ring segments was considered to be more useful; however, the rings fabricated from monofilaments in the organic finish phase of this program were not sufficiently thick for the required testing. During the final portion of the study, 60-mil thick rings were produced and interlaminar shear strength tests were successfully performed. This is reported in later sections of this report.

41

B. TENSILE STRENGTH OF COMPOSITE STRUCTURES

The final evaluation procedure for organic glass coatings in composite structures was the tensile strength testing of NOL rings. Test conditions were in accordance with NOL specifications except for thickness, which is specified as 0.125 ± 0.003 inch. A floor model Instron Universal Tester with a maximum limit of 11,000 pounds was used along with a standard NOL split-ring tensile jig, in accordance with NOL specifications (Figure 18). Cryogenic tensile tests were performed with an insulated chamber in which the split-D of the tensile fixture was mounted. Hoops were mounted on a split-D fixture and immersed in the liquid nitrogen for one-half hour before testing.

The results are shown in Tables 12 to 14 and summarized in Table 15. The results have been discussed in Section I of this report.

C. THERMAL SHOCK

Thermal shock tests were performed by immersing the specimen in liquid nitrogen for ten minutes, removing and then conditioning for one hour at ambient conditions prior to testing. Both tensile and interlaminar tests were performed on samples which had been thermal shocked. The results are reported in Tables 12, 13, 14, 15 and 18.

42

TABLE 11

FLEXURAL STRENGTH PROPERTIES OF NOL RING SEGMENTS

Control--No Finish

Ring No.	13B	14B	15B	25B	26B	Average
Dry (ksi)	179	154	142	93.4	122	138
Wet (ksi)*	130	134	65.5	--	101	108

Buton-Silane Epoxy Finish

Ring No.	32BB	33BB	34BB	36BB	37BB	Average
Dry (ksi)	150	182	111	134	--	144
Wet (ksi)	109	124	--	--	--	116

Urethane Finish

Ring No.	40BU	49BU	52BU	2BU	3BU	Average
Dry (ksi)	76.5	128	67.5	143	203	124
Wet (ksi)	19.7	20.9	19.9	32.6	29.5	24.7

*
The wet tests were performed by boiling the sample for two hours, rinsing, drying by wiping and conditioning at 50% R.H.-70°F for 24 hours.

43

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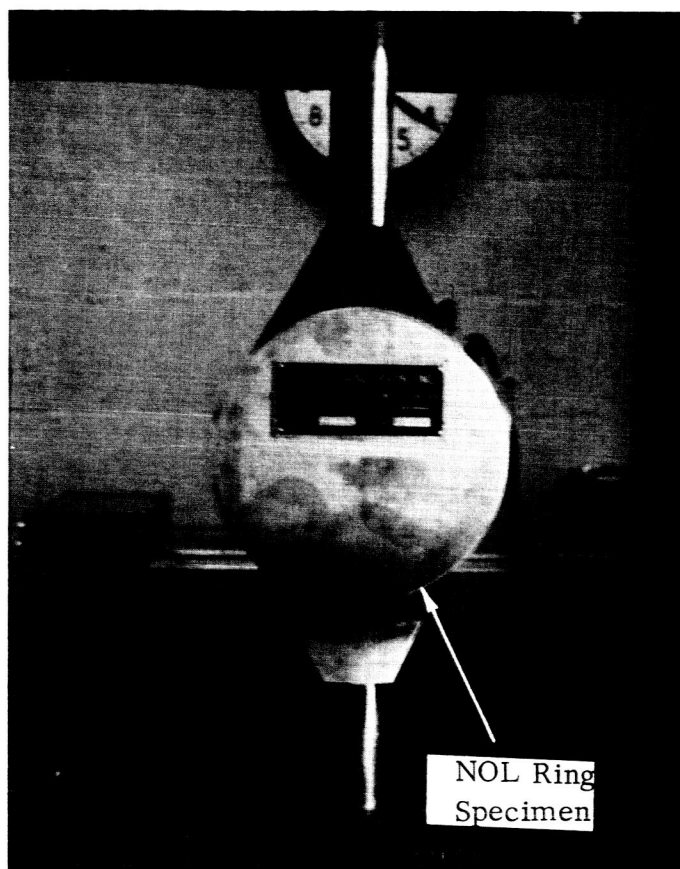
NOL Ring
Specimen

FIGURE 18   SPLIT-D TEST FIXTURE
MOUNTED WITH NOL
RING SPECIMEN

TABLE 12

TENSILE STRENGTH OF NOL CONTROL RINGS (UNCOATED)
(ksi)

	13B	14B	15B	16B	25B	26B	Average	Standard Deviation
Tensile Strength (RT)	214	194	173	191	211	234	203	21.5
Tensile Strength (-320°F)	236	202	258	264	133	208	217	46.7
Two-hr Boil (RT)	47	116	129	104	58	128	97	32.8
Two-hr Boil (-320°F)	- -	115	195	100	- -	233	161	19.8
Thermal Shock	197	212	152	106	65	171	151	18.6
Resin Content (% by wt)	12.5	12.3	8.5	12.2	9.53	14.2	11.54	2.37
Void Content (% by vol)	6.45	8.4	11.7	4.3	12.0	22	10.81	6.37
Density (Composite)	2.08 g/cc	2.08 g/cc	2.05 g/cc	2.05 g/cc	2.02 g/cc	1.71 g/cc	2.01	0.3

45

TABLE 13

TENSILE STRENGTH OF BUTON-SILANE EPOXY-FINISHED NOL RINGS

(ksi)

	32BB	33BB	34BB	36BB	37B	Average	Standard Deviation
Tensile Strength (RT)	293	223	216	183	205	224	42.5
Tensile Strength (-320°F)	197	262	170	197	250	215	47.4
Two-hr Boil (RT)	158	151	108	140	128	137	54.8
Two-hr Boil (-320°F)	219	170	127	--	147	166	69.3
Thermal Shock	195	165	137	210	173	174	41.3
Resin Content (% by wt)*	13.3	11.8	13.5	10.7	11.4	12.1	1.58
Void Content (% by vol)	9.4	11.5	3.4	12.2	23.6	12.0	7.3
Density (Composite)	2.0 g/cc	1.98 g/cc	2.13 g/cc	1.99 g/cc	1.98 g/cc	2.02 g/cc	0.27 g/cc

*Including finish.

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TABLE 14

TENSILE STRENGTH OF URETHANE EPOXY-FINISHED NOL RINGS
(ksi)

	40BU	49BU	52BU	3BU	Average	Standard Deviation
Tensile Strength (RT)	250	215	181	205	213	20.0
Tensile Strength (-320°F)	112	125	95.5	204	134	45.0
Two-hr Boil (RT)	- -	- -	66.5	117	92	15.8
Two-hr Boil (-320°F)	- -	- -	- -	161	161	- -
Thermal Shock	145	157	143	208	164	28
Resin (% by wt)*	18.8	11.07	8.62	15.6	13.86	3.8
Voids (% by vol)	8.8	2.82	20.2	10.1	9.97	6.2
Density (Composite)	1.91 g/cc	2.2 g/cc	1.85 g/cc	1.93 g/cc	1.98 g/cc	0.2

*Including finish.

47

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TABLE 15

SUMMARY OF TENSILE STRENGTHS OF ORGANIC-FINISHED NOL RINGS
(ksi)

	Control--No Finish		Buton-Silane Epoxy Finish		Urethane Finish	
	Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Tensile Strength (RT)	203	21.5	224	42.5	213	20.0
Tensile Strength (-320°F)	217	46.7	215	47.4	134	45.0
Boil Test (RT)	97	32.8	137	54.8	92	15.8
Boil Test (-320°F)	161	19.8	166	69.3	161	--
Thermal Shock	151	18.6	174	-41.3	164	28
Resin Content (% by wt)*	11.5	2.37	12.1	1.58	13.86	3.87
Void Content (% by vol)	10.81	.6.37	12.0	7.37	9.97	6.2
Density (Composite)	2.01 g/cc	0.32 g/cc	2.02 g/cc	0.27 g/cc	1.98 g/cc	0.2 g/cc

*Including finish where applicable.

48

VII. FABRICATION AND TESTING OF NICKEL-COATED GLASS MONOFILAMENT-WOUND NOL RINGS

In order to fabricate nickel-coated glass NOL rings the process and facility for continuous nickel-coating described in Section III were developed. The coating experiments are described in the following. At first it was thought that the drawing speeds would have to be kept fairly low (about 300 ft/min or less) if satisfactory coating thicknesses were to be obtained. Accordingly, a glass melting furnace was fabricated with a smaller diameter orifice (0.035-inch compared to the 0.050-inch furnace used in the previous organic-finish work). It was found, however, that this smaller orifice did not produce acceptable 10-micron glass at 300 ft/min drawing speeds. Therefore, the standard furnace was used in subsequent work.

A. APPLICATION OF NICKEL TO GLASS

In applying the nickel to the glass in the continuous drawing process, a series of experimental runs was made to determine the conditions by which a coherent layer of metal could be applied to the filament. Since the analysis of the metal required several days, the coatings were visually examined during application. (See Figures 19 and 20.) Although we did not conduct an exhaustive study, we can draw some general conclusions from the limited number of runs which may be helpful in future work.

Table 16 describes the nickel-coating conditions and the percentage of nickel applied as determined by subsequent analysis. For example, in start-up runs 3, 5 and 6 the glass-drawing speeds were started at a low of 120 ft/min and increased to 270, and finally to 540 ft/min. At an Argon chamber temperature of 530 to 550°F and at these low speeds 0.42 to 0.64 part by weight of nickel was deposited on the glass fibers. At an upper chamber temperature of about 570 to 580°F and at drawing speeds of about 800 ft/min (Runs 12 to 15) about 1.19 parts by weight of nickel ($\sim 100\text{\AA}$ thick) were deposited. Some trouble developed during runs 16 to 19, which was definitely established as stemming from thermocouple difficulties. Nickel deposits formed at the holes in the graphite separators separating the Argon chamber from the carbonyl chamber. During the filament drawing, numerous breaks were also encountered. Judging from the increased deposition weight (2 to 2.3%) and the nickel deposit at the graphite inserts, it must be assumed that the temperature in the Argon chamber was higher than that recorded. After the thermocouple had been repaired, final runs 20 to 22 were made at an Argon chamber temperature of 550-570°F. This resulted in much lower deposits ($\sim$.3%) which, however, still appeared to be uniform and coherent.
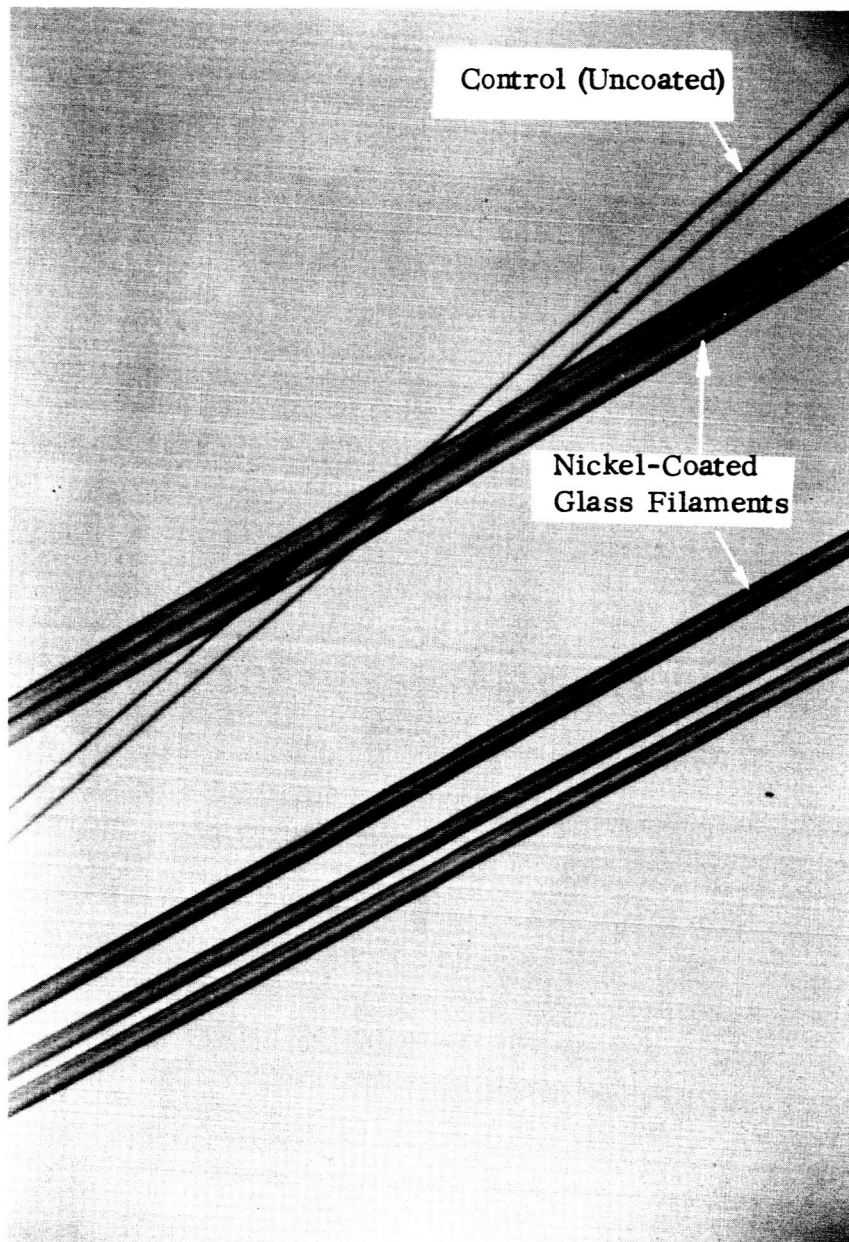
FIGURE 19   NICKEL-COATED GLASS FILAMENTS
              COMPARED WITH UNCOATED CONTROL
              (200X)

Nickel-
Coated
Filament
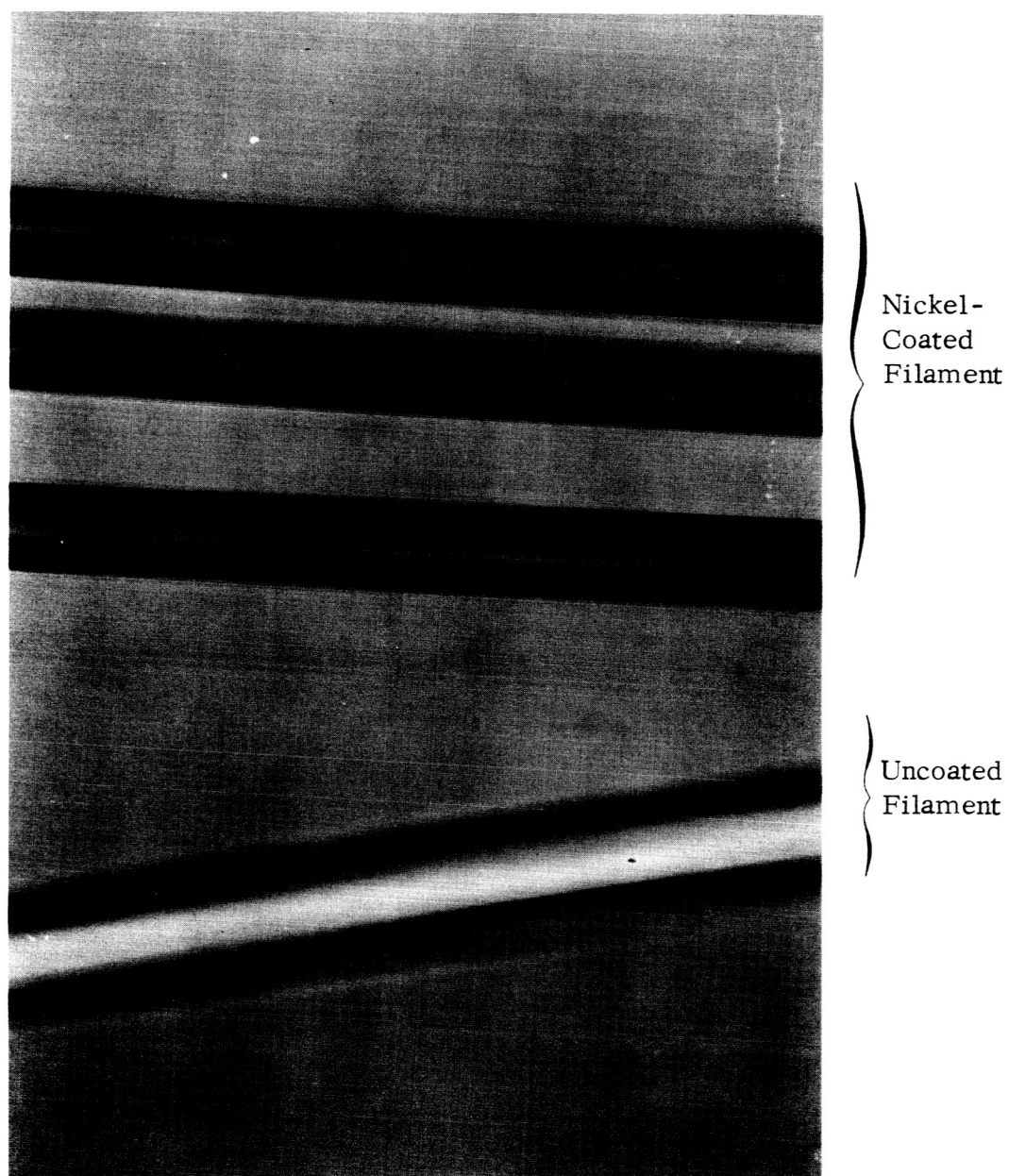
Uncoated
Filament

FIGURE 20   NICKEL-COATED GLASS FILAMENTS
COMPARED WITH UNCOATED CONTROL
(800X)

TABLE 16

COATING CONDITIONS

A. Nickel-Coating Conditions

Sample No.	Percent Nickel Deposited (by weight)	Argon Chamber Furnace Temp. (°F)	Glass Drawing Speed (ft/min)
Start-up Runs			
3	0.45	530	120
5	0.42	530-580	270
6	0.64	550	540
Test Runs			
12	1.19	580	775
13	1.19	580	775
14	1.19	570	825
15	1.19	570**	815
16	2.01	580**	750
17	2.01	580	735
18	2.33	580	825
19	2.33	608	785
20	0.29	550-560	765
21	0.29	550-570	765
22*	0.31	560-570	795
B. Control Ring Conditions			
1	-	-	240
23	-	-	790
24*	-	-	790
25*	-	-	790

*Cylinders wider than NOL rings were fabricated.

**Recorded temps. probably too low since thermocouple trouble definitely established at run 19.

In spite of the preliminary nature of these experiments it appears that continuous nickel coating from carbonyl during monofilament glass drawing is both feasible and practical. It is believed that uniform coherent coatings could be readily achieved at greater drawing speeds. This might necessitate higher Argon chamber temperatures and some measure to avoid metal deposition at the graphite separators. Possibly this could be achieved by cooling the orifices, for example, by replacing the graphite separators with carbon- or graphite-coated tubing which could be water-cooled.

Figure 21 is an electron microphotograph of the top section of an uncoated glass filament cross section embedded in phenolic resin (magnification 29,500 X). Figure 22 is the electron microphotograph of the top section of a coated glass filament cross section embedded in phenolic resin (magnification 29,500 X). The dark area in the photograph, as indicated, shows what appears to be the nickel coating. In this particular view, the coating thickness measures about 150 angstroms. Figures 20 and 21 (electron microphotographs) were obtained by NASA-Lewis Research Center.

B. FABRICATION OF NICKEL-COATED NOL RINGS

In the "test runs," other than 22, 24, and 25, single NOL rings were fabricated using the standard Naval Ordnance Laboratory mold described for the split-D tensile tests. The epoxy composition (Section V) was applied by felt and metered by means of a Teflon finger which monitored the traverse of the coated glass. The fabrication of the rings required 60-90 minutes, depending upon drawing speed,to provide an approximate 60-mil thickness.

The mold was placed in an oven and the rings were cured at 85°C for four hours and then at 125°C for two hours. The mold was removed from the oven and cooled, and the rings removed by placing the mold in a dry ice-acetone bath to cool and shrink the metal mold, thus allowing the rings to be removed easily. The tops of the rings were faced off slightly with a machine cutting tool to insure uniform thickness. (See Figure 23.)

Several 1" and 1-1/4" wide cylinders were also prepared on the mandrel used in previous organic coating work, and a wider cylinder was made by adjustment of the traversing mechanism. Although the cylinders took longer to prepare, we successfully prepared control and nickel cylinders approximately 50 mils thick. The cylinders were machined on the surface to a uniform thickness of not less than 40 mils and cut into 1/4" wide rings.

53

FIGURE 21   UNCOATED E-GLASS (29,500X)

FIGURE 22   NICKEL-COATED E-GLASS FILAMENT (150 Å THICKNESS) (29,500X)
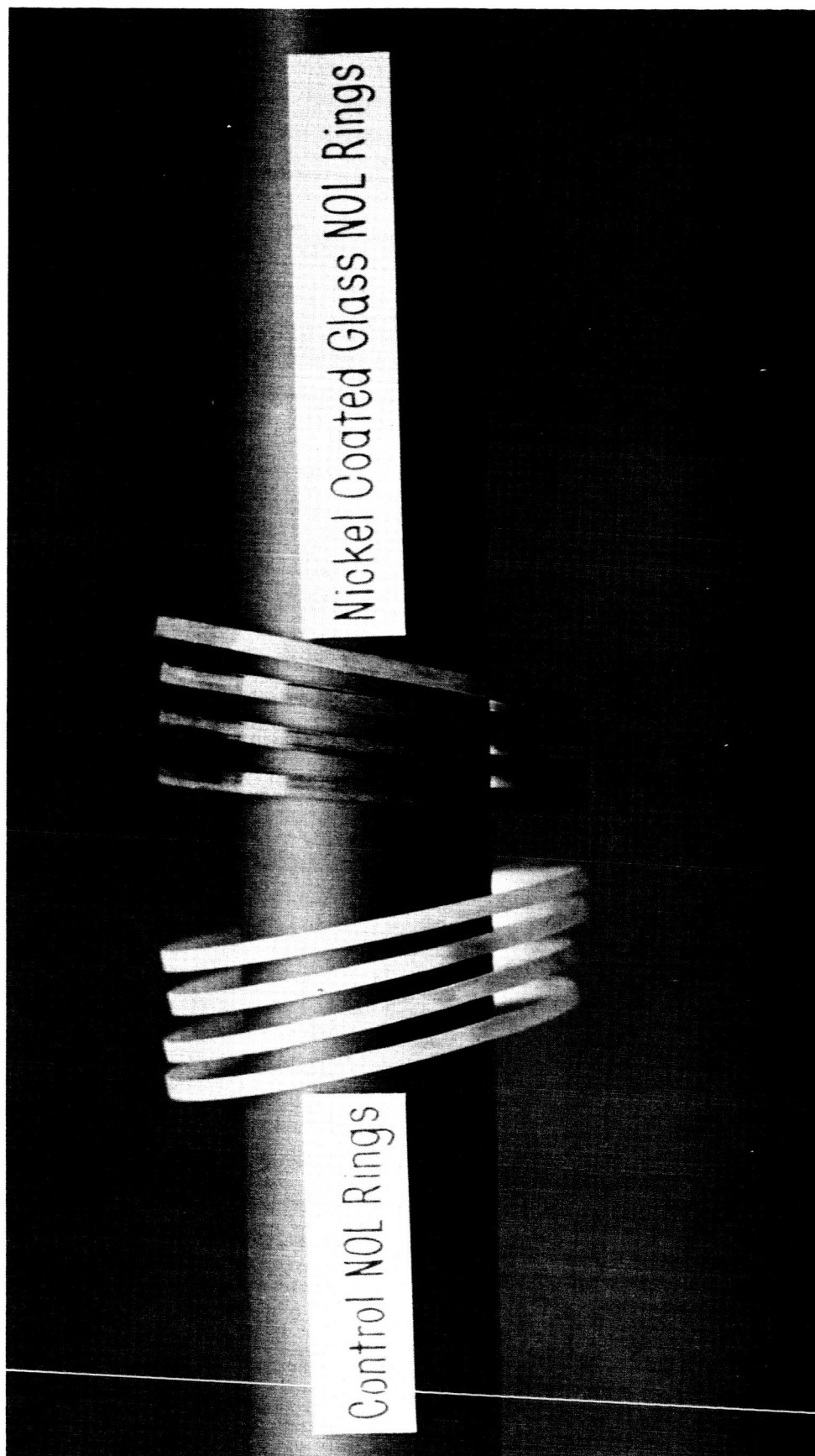
FIGURE 23   NICKEL-COATED RINGS COMPARED WITH CONTROL

C. EVALUATION OF NICKEL COATINGS

1. Interlaminar Shear

Rings prepared on the single-NOL ring mold were surfaced with a machine tool to a thickness of 0.06 inch (as measured from the inside diameter). The rings were then cut into pieces one inch long with a diamond saw, exposing the glass filament in cross section at the ends. The pieces were then tested for interlaminar shear using a fixture similar to a design described by W. Eakins.[1] The specimens were tested at a span-to-depth ratio of 8 to 1 using three 1/4-inch diameter bars. A test piece was inserted so that the middle or loading bar rested on the inside or convex portion of the ring. Failure in interlaminar shear occurs approximately midway between the upper and lower faces of the specimen. If the glass content and resin thickness are not factors, the mechanism of shear must be in the interface area. This test, therefore, provides an excellent method of determining the soundness of the protective coating on the glass. Calculations were performed as follows:

$$\text{Horizontal shear} = \frac{0.75p}{bd}$$

where:

P = breaking load (pounds or grams)

b = width (inches or centimeters)

d = thickness (inches or centimeters)

The following split-D tensile tests were performed on the 40- to 50-mil thick NOL rings: (1) room temperature, (2) two-hour boil and test at room temperature, and (3) test at cryogenic temperature (-320°F).

Table 17 is a summary of these tests. The void content in this table was based on rings that were destroyed in the test.

Tests were made under the following conditions: (1) room temperature, (2) after five-hour boil at room temperature, (3) immersing sample in liquid nitrogen for ten minutes (thermal shock), removing, allowing to condition to room temperature and testing at room temperature, and (4) at cryogenic temperatures (-320°F).

---

[1]SPE Journal, Vol. 19 (6).

57

TABLE 17

TENSILE STRENGTH OF NICKEL-COATED NOL RINGS

Ring No.*	Nickel Coating (% by wt.)	Void Content (% by vol.)	Resin Content (% by wt.)	Tensile Strength (psi)	Remarks
25-A	Control	2.3	13.2	197,000	Room Temp.
25-B	Control	-	-	175,000	
25-C	Control	-	-	179,000	
25-D	Control	-	-	189,000	
				185,000 (average)	
24-A	Control	5.4	12.5	150,000	
24-C**	Control	9.1	12.8	51,400	After Boil
1***	Control	4.6	14.6	107,000	
24-B	Control	6.6	13.0	195,000	Cryo (-320°F)
22-A	0.29	14.8	12.3	175,000	Room Temp.
14***	1.19	1.3	13.4	183,000	
18***	2.33	2.5	14.9	160,000	
22-C	0.29	14.4	12.9	130,000	After Boil
16***	2.01	0	14.7	153,000	
20***	0.31	2.4	12.9	153,000	
22-B	0.29	14.4	12.9	217,000	Cryo (-320°F)
15***	1.19	0	13.2	236,000	
19***	2.33	7.7	13.8	298,000	

*Rings coded A, B, C, and D were prepared from cylinders (sectioned into 1/4" wide rings).

**Sample 24-C distorted on boiling and was difficult to fit into split-D fixture which may account for low value.

***Rings prepared on single-NOL ring mold.

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Results are shown in Table 18. Control and nickel rings behaved quite similarly on thermal shock and at cryogenic temperatures. The five-hour boil test, however, does show significant differences between control and nickel rings. For example, after boil, control rings (no finish) show a strength retention of about 20% while nickel rings show a strength retention of about 40%.

On the basis of these boil tests, additional samples were tested at various periods of boiling in an effort to determine the effectiveness of the nickel coating under extended exposure to moisture. Table 19 shows these additional tests with a nickel-coated ring containing 1.19% nickel by weight. Interlaminar shear strength results were obtained on "as is," half-hour boil, and two-hour boil.

As can be seen from the table, the half-hour samples retain about 90% of their original strength, and after drying appear to be even somewhat stronger. Three-hour boil samples retained 35-40% of their original strength; after drying this figure increased to about 45%, similar to the five-hour boil samples in the preceding list.

For further comparison a series of rings was also prepared with a simulated HTS-finish and the Araldite 6005-Catalyst CL resin binder. HTS-simulated finish was applied directly to the glass during drawing in a manner similar to that used with the organic treatments. The finish was dissolved in solvent and a dry coating of 2% by weight (based on the glass) was applied to the glass filament during drawing. The Araldite 6005- Araldite RD-2, Catalyst CL was next applied to the simulated HTS-finish glass and single-cylinder NOL rings were fabricated.

The rings were cured in the same manner as previous rings (2 hours at 85°C; 4 hours at 125°C). They were then cut into one-inch long specimens and tested for interlaminar shear strength under the following conditions:

> Ambient temperature
>
> 3-hour boil, 3-hour dry
>
> 5-hour boil, 5-hour dry
>
> 24-hour boil

The test results shown in Table 20 indicate that 86% of the original strength is retained after three-hour boil with 90% strength retention after drying; and 86% strength retention after five-hour boil with 80% strength retention after drying. Twenty-four hour boiling results in a strength retention of 81%. The 86% strength retention after five-hour boiling of the "HTS-Simulated" finish is higher than the 19.1% of the "no finish" control, and 41.6% of the nickel-coated glass.

59

TABLE 18

INTERLAMINAR SHEAR STRENGTH TESTS (psi)
(Nickel and Control NOL Rings)

Test Condition: Room Temperature (73°F)
(No void content available)

Control Ring #23	Nickel Ring #21*	Percent Retention Based on Initial Tests at Room Temperature	
		Control Ring	Nickel Ring
No Finish			
(1) 13,900	(1) 11,200	23-1	21-1
(2) 12,600	(2) 8,500**		
(3) 12,400	(3) 11,400	100%	100%
(4) 12,800	(4) 11,400		
12,925 (average)	11,333 (average)		
Thermal Shock			
(1) 13,300	(1) 11,500		
(2) 13,000	(2) 10,900	104%	100%
(3) 13,400	(3) 11,300		
(4) 14,000	(4) 11,600		
13,425 (average)	11,333 (average)		
Cryo (-320°F)			
(1) 22,400	(1) 15,200		
(2) 19,400	(2) 16,600	146%	150%
(3) 15,600	(3) 16,900		
(4) 17,900	(4) 19,000		
18,825 (average)	16,925 (average)		
Five-Hour Boil			
(1) 2,150	(1) 4,860	19.1%	41.6%
(2) 2,340	(2) 4,600		
2,245 (average)	4,730 (average)		

*Ni = 0.29%.
**Poor specimen; did not produce a true shear; omitted from average.

60

TABLE 19

INTERLAMINAR SHEAR STRENGTH TESTS - ADDITIONAL BOIL TESTS ON NICKEL-COATED NOL RING #13
(1.19% Nickel by Weight)
(Void Content - 1.32%)
(in psi)

1. **No. Boil**

    10,650
    11,500
    10,800

    Average: 10,983

2. **Boil One-Half Hour** (tested as is)

    10,000   91.5% original strength retention
    10,200
     9,850

    Average: 10,000

3. **Boil Three Hours** (tested as is)

    3,860   36.8% original strength retention
    4,160
    4,100

    Average: 4,040

4. **Boil One-Half Hour, Dried One-Half Hour**

    10,400   94.5% original strength retention
     9,500
    10,200

    Average: 10,030

5. **Boil Three Hours, Dried Three Hours**

    4,920   44.2% original strength retention
    4,820
    4,750

    Average: 4,830

61

TABLE 20

INTERLAMINAR SHEAR STRENGTH TESTS--NOL RINGS
PREPARED WITH "HTS-SIMULATED" FINISH
(in psi)

Room Temperature

    8,670
    9,260
    <u>8,730</u>

    8,886 - average

3-Hr Boil, No Dry	3-Hr Boil, 3-Hr Dry 150°F
7,620	8,150
7,680	7,960
<u>7,620</u>	<u>8,150</u>
7,640 - average 86% strength retention	8,087 - average 90% strength retention

5-Hr Boil, No Dry	5-Hr Boil, 5-Hr Dry 150°F
7,700	7,030
7,080	7,300
<u>7,160</u>	<u>7,000</u>
7,646 - average 86% strength retention	7,110 - average 80% strength retention

24-Hr Boil

    7,260 - 81% strength retention

Conceivably, addition of 1-5% silicone (α-aminopropyl silane) (Union Carbide's A-1100) based on the total epoxy resin binder might help further improve the moisture resistance of the nickel-coated specimens. It is evident that the application of nickel in the described quantities does not provide the necessary moisture resistance in the composite ring; therefore, further consideration should be given to any advantages that may be gained by combining the metal finish with a silicone additive to provide an improved resin matrix.

2. Moisture Absorption

Nickel and control samples, made of NOL ring segments, were boiled for five hours during which they were removed periodically and weighed to determine the amount and rate of water pickup. Figure 24 shows the rate of water pickup by control samples both with no finish and an HTS-simulated finish, and by nickel NOL ring samples 13 and 21 containing 1.19% and 0.29% nickel, respectively. This shows that the nickel and HTS-finish NOL ring samples reach an equilibrium of 0.3% by weight in one hour, whereas the control reaches the maximum pickup at five hours and equilibrium of 4.3% at the end of 24 hours.

Figure 25 represents the same curves as in Figure 24 except they are expressed as percent of resin content. Again, the figure, showing the rate of water pickup expressed as percent of resin content, indicates that the nickel NOL ring and the simulated HTS-finish samples reached equilibrium at the end of one hour.

Obviously, the higher percentage values calculated for the "no finish" control cannot be attributed to swelling of the resin. As shown in Figure 26, this sample is visibly fibrilated, and the high water pickup is due to the opening of spaces in the disintegrating sample. The control (HTS) and nickel-coated samples appear structurally unchanged after the 24-hour boil test. This demonstrates that the application of nickel to the glass filament during drawing, even at percentages as low as 0.29% by weight, appears to protect the bare glass filaments from moisture degradation.

In order to determine the effect of moisture on the epoxy system (ARALDITE 6005 - ARALDITE RD-2, and Catalyst CL), specimens (1" long, 1/2" wide, and .050" thick) were boiled in water for the same periods of time as the one-inch long ring specimens. As also shown in Figure 25, water pickup is slower than in the composites, but has not reached equilibrium after 24 hours.

63
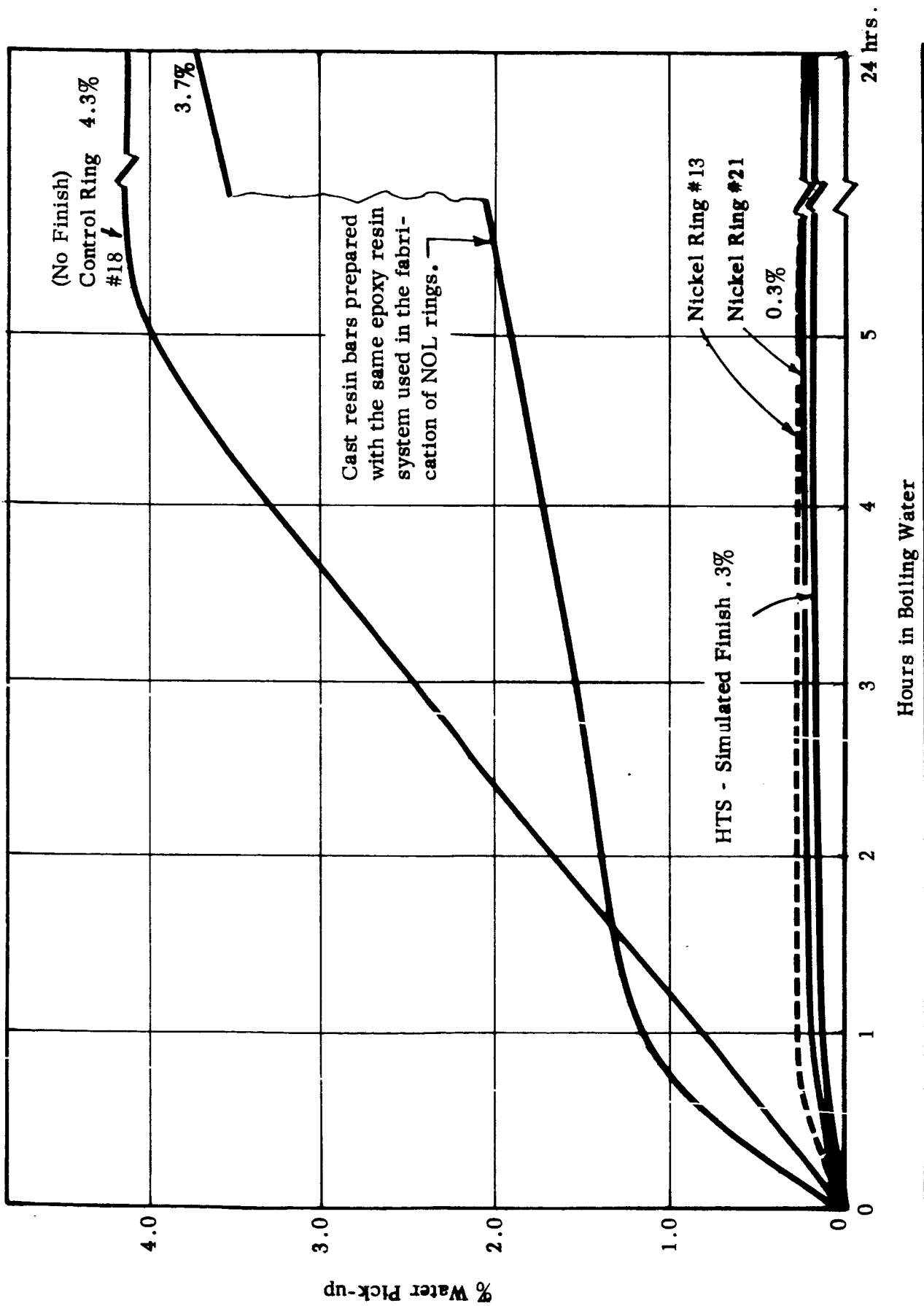
FIGURE 24 . BOIL TESTS ON NICKEL AND CONTROL SPECIMENS (PERCENT WATER PICKUP)

64
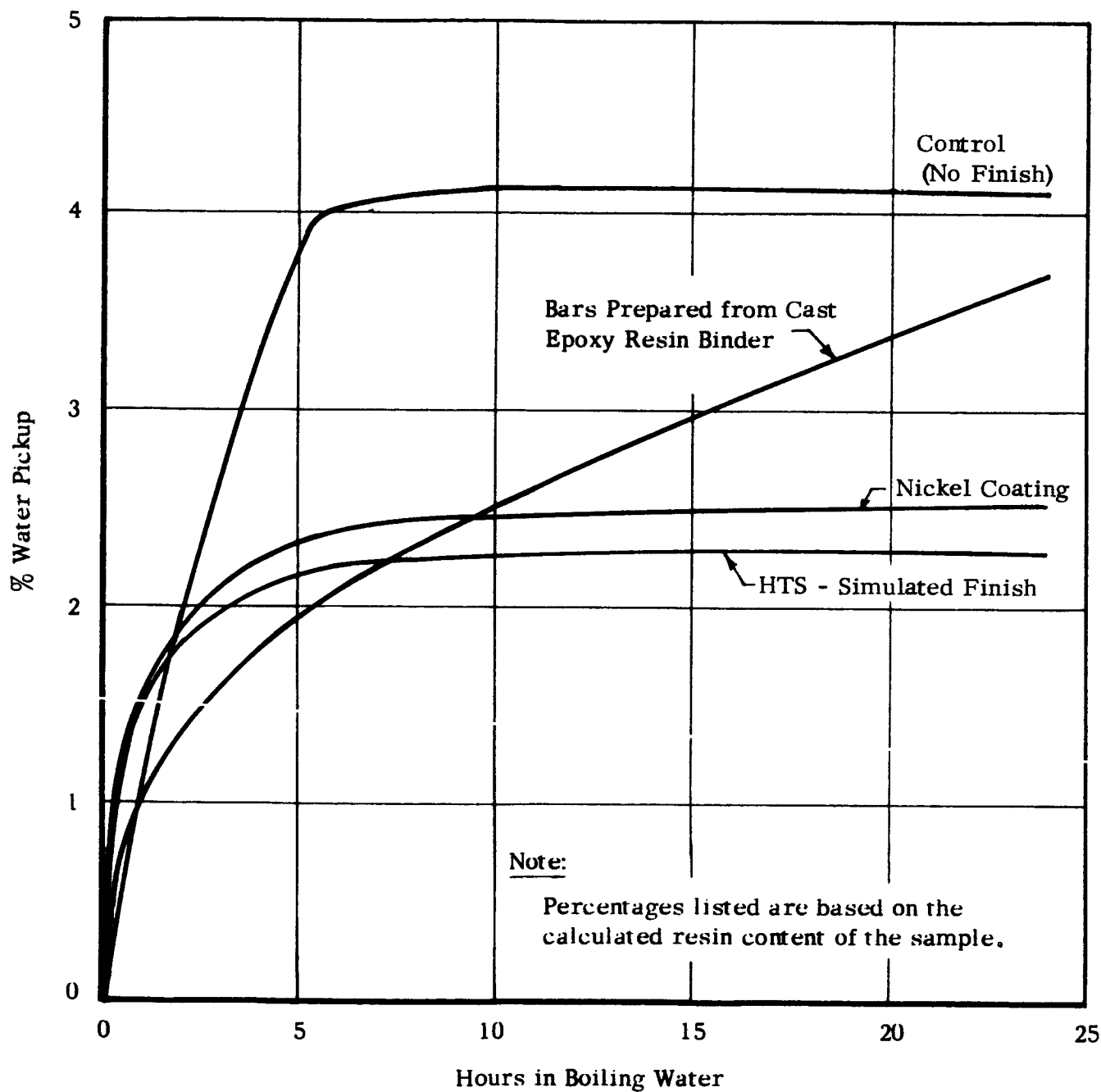
FIGURE 25   BOIL TESTS ON NICKEL AND CONTROL SPECIMENS BASED ON RESIN CONTENT

65

No Finish

Nickel Finish

HTS-Simulated Finish
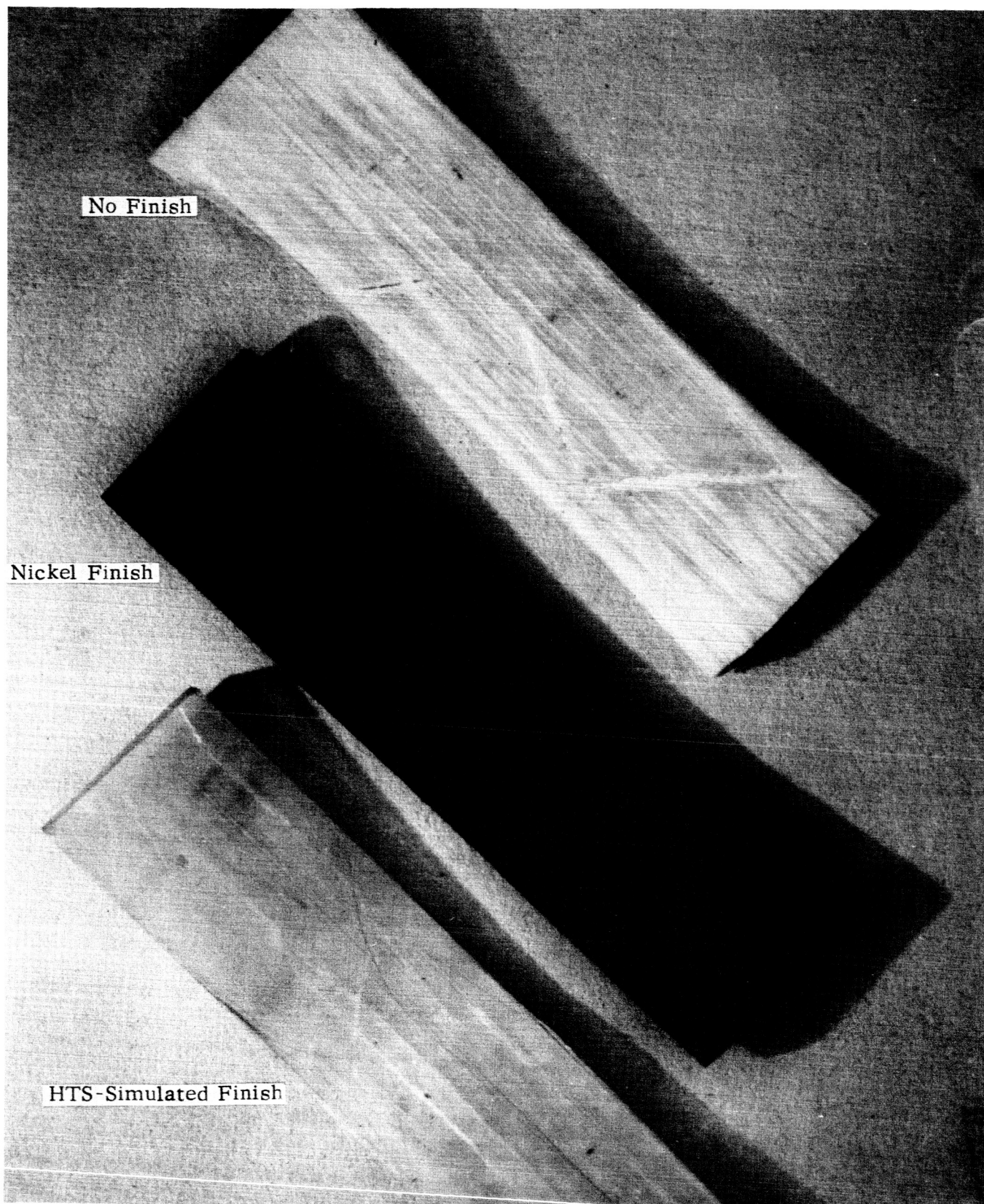
FIGURE 26   24-HOUR BOIL TESTS ON NICKEL AND CONTROL SAMPLES

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